Materials for Magnetic Recording Applications

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Abstract

In the first part of this work, the influence of hydrogen on the structural and magnetic properties of Fe/V(001) superlattices was studied. The local structure of the vanadium-hydride layers was determined by extended x-ray absorption fine structure (EXAFS) measurements. The magnetic ordering in a weakly coupled Fe/V(001) superlattice was investigated using the magneto-optical Kerr effect (MOKE). The interlayer exchange coupling is weakened upon alloying with hydrogen and a phase with short-range magnetic order was observed.

The second part is concerned with first-principles calculations of magnetic materials, with a focus on magnetic recording applications. The uniaxial magnetic anisotropy energy (MAE) of Fe, Co, and Ni was calculated for tetragonal and trigonal structures. Based on an analysis of the electronic states of tetragonal Fe and Co at the center of the Brillouin zone, tetragonal Fe-Co alloys were proposed as a material that combines a large uniaxial MAE with a large saturation magnetization. This was confirmed by experimental studies on (Fe,Co)/Pt superlattices. The large uniaxial MAE of L11 FePt is caused by the large spin-orbit interaction on the Pt sites in connection with a strong hybridization between Fe and Pt. Furthermore, it was shown that the uniaxial MAE can be increased by alloying the Fe sublattice with Mn. The combination of the high-moment rare-earth (RE) metals with the high-Tc 3d transition metals in RE/Cr/Fe multilayers (RE = Gd, Tb, Dy) gives rise to a strong ferromagnetic effective exchange interaction between the Fe layers and the RE layer. The MAE of hcp Gd was found to have two principal contributions, namely the dipole interaction of the large localized 4f spins and the band electron magnetic anisotropy due to the spin-orbit interaction. The peculiar temperature dependence of the easy axis of magnetization was reproduced on a qualitative level.

Keywords: magnetic materials, magnetic anisotropy, saturation magnetization, magnetic data storage, superlattice, hydrogen, density functional theory, first-principles calculations, two-dimensional magnetism, FP-LMTO, EXAFS, MOKE

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vackert land vi bor i

Bo Kaspers morfar i bilen på väg ut till stugan minst två gånger milen.
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


VII Magnetic properties of Fe/Co(001) superlattices from first-principles theory A. Bergman, T. Burkert, B. Sanyal, S. Frota-Pessôa, L. Nordström, and O. Eriksson, in manuscript

VIII Multilayers of rare-earth and transition metals—a high moment magnetic material B. Sanyal, T. Burkert, O. Eriksson, and O. Heinonen, in manuscript
IX  Theory of the temperature dependence of the easy axis of magnetization in hcp Gd

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The following articles are coauthored by me but not included in the thesis.

X  Magnetic anisotropy from electronic structure calculations

XI  Cycloidal magnetic order in the new phase IrMnSi
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1. Introduction

During the last decades the focus of research on magnetic materials has shifted from bulk materials to surfaces, artificially layered materials, and nanostructures. The properties of these new types of materials are dominated by surfaces and interfaces, chemical modulation, finite-size effects, and reduced dimensionality in one or more dimensions. This development emerged as a natural step once the technological prerequisites allowed the tailoring of artificial materials on an atomic level. Parallel to the development of experimental techniques it was the steadily increasing performance of computers that, together with the developments of density functional theory and related computational methods, allowed to conduct first-principles calculations of materials that contributed both to the understanding of materials properties and their design.

Even from a technological point of view the enforced efforts on research of advanced magnetic materials has been fruitful. Only ten years after the discovery of the interlayer exchange coupling and the related giant magneto-resistance (GMR) in magnetic multilayers, GMR sensors were routinely used in computer hard disk drives. The vast part of information storage that our daily life relies on is based on magnetic data storage, and new materials with improved properties for hard disk drives—both media materials and read/write heads—are continuously sought after. Novel, miniaturized devices are nowadays based on materials which are dominated by the before-mentioned properties that are absent in bulk materials. It is the miniaturization itself that called for a better understanding of these properties when the devices were reduced to such an extent that their finite size influenced the physical properties.

The research presented in this thesis can be divided into two parts. The first part is an experimental work of more fundamental character and is based on Fe/V(001) superlattices that serve as a model system to study the influence of dimensionality on magnetism. In Paper I the local structure of the V layers is investigated as a function of alloying with hydrogen, which is used to modify the interlayer exchange coupling between the magnetic Fe layers. Under certain conditions this coupling can be made sufficiently weak, so that the sample behaves as a collection of quasi-two-dimensional magnets. This was studied in Paper II.

The second part involves first-principles calculations of magnetic materials. The focus is on the magnetic anisotropy, which is a technologically relevant
property of magnetic materials. In Paper III the magnetic anisotropy of Fe, Co, and Ni is studied for strained structures that can occur in epitaxial growth. As an extension to this, the magnetic anisotropy of tetragonal Fe-Co alloys is studied in Papers IV and V, exploiting the alloy composition as an additional parameter in materials design. In Paper VI the magnetic anisotropy of FePt, a possible candidate for magnetic data storage applications, and its alloys with Mn is studied. The subject of Papers VII and VIII is materials with large saturation magnetic moments, and correspondingly large saturation fields, which is an important property in the context of magnetic recording applications. The magnetic anisotropy of hcp Gd has been a long-standing problem of more fundamental than technological interest and is discussed in Paper IX.

The purpose of this introductory part is to supply the background necessary to understand the physical concepts and methods presented in the publications contained in this thesis, as well as to point out relevant literature. It is aimed at a reader with basic knowledge in condensed matter physics and quantum mechanics. The selection of topics presented here is, of course, biased by what I consider to be relevant and hence far from complete. Chapter 2 is devoted to the experimental work of this thesis and covers the most important techniques that I used and gives a short introduction to the dimensionality aspects of magnetism. In Chapter 3 density functional theory is presented, together with the Kohn-Sham approach and the LMTO method, which is the basis for most of the calculations done in this work. The subject of Chapter 4 is magnetic materials and the calculation of their properties from first principles, with a focus on magnetic data storage and magnetic anisotropy. Finally, conclusions and an outlook are given in Chapter 5.
2. Fe/VH₄(001) superlattices: Local structure and quasi-two-dimensional magnetism

This chapter provides the background to Papers I and II, in which Fe/V(001) superlattices were studied. First, some relevant properties of Fe/V(001) superlattices will be summarized. Then, in Section 2.2, the EXAFS technique is presented, which was used to study the local structure of the V layers in these superlattices upon alloying with hydrogen in Paper I. The last two sections are devoted to Paper II, which reports on the realization of a quasi-two-dimensional magnetic phase in these superlattices. Section 2.3 gives a brief introduction to the dimensionality aspects of magnetism, and the MOKE technique will be presented in Section 2.4. A summary of Papers I and II is given in Section 2.5.

2.1 Fe/V(001) superlattices

A superlattice is a periodically layered structure of single-crystalline nature, i.e., with a structural coherence both in the film plane and perpendicular to it. The out-of-plane coherence length is much larger than the period \( \Lambda = d_{Fe} + d_{V} \) of the superlattice, where \( d_{Fe} \) and \( d_{V} \) denote the thicknesses of the individual layers within each period of the stack. Typically, a superlattice consists of 10 to 100 periods. In the notation \([Fe_{n}/V_{m}(001)]_{N}\) that is commonly used in connection with superlattices, \( n \) and \( m \) denote the number of monolayers (ML) in each of the \( N \) periods.

Fe/V(001) superlattices are grown by dc magnetron sputtering in ultra-high vacuum (UHV) based equipment using Ar as a sputter gas. The samples used in this work were grown epitaxially on MgO(001) single-crystal substrates in the temperature range 300–330°C at a growth rate of typically 0.3–0.5 Å/s. Details of the growth procedure and the sputtering equipment can be found in Ref. [1]. The lattice mismatch of 5.4% between bulk Fe and V results in a tetragonally strained structure with body-centered tetragonal (bct) unit cells. The in-plane biaxial strain is compressive in the V layers and tensile in the Fe layers and depends on the ratio \( d_{Fe}/d_{V} \) as well as the elastic constants of Fe and V.
Figure 2.1: Sketch of an octahedral \( z \) site (open circle) in a bcc host lattice. The arrows indicate the displacement of the neighboring atoms.

The structural properties of these superlattices were investigated by x-ray diffraction (XRD) and x-ray reflectivity. XRD is sensitive to the structural order on an atomic scale. It confirms the single-crystalline nature of the superlattice and yields information about the average out-of-plane lattice parameter, the mosaicity, and the strain state of the sample. X-ray reflectivity, on the other hand, yields information about the chemical modulation of the structure and can be used to evaluate how well the thicknesses of the individual layers are defined throughout the superlattice and if the total thickness of the stack is well defined within the region probed by the beam. X-ray analysis serves as a simple and powerful tool to determine the structural properties after the growth of the sample. The varying structural quality of a series of samples grown under different conditions can be established by merely comparing their x-ray diffraction and reflectivity results. A more quantitative analysis can be performed by simulation of the x-ray diffraction and reflectivity. More detailed descriptions of the application of x-ray analysis to thin films and heterostructures have been given by Fewster [2] and Zabel [3].

The V layers in Fe/V(001) superlattices can be alloyed with hydrogen simply by exposing the sample to hydrogen gas. Usually a Pd capping layer is used that enhances the dissociation and uptake of hydrogen. Because the heat of solution of hydrogen is exothermic for V and endothermic for Fe, only the V layers absorb hydrogen, apart from two to three monolayers at each V-Fe interface that are depleted of hydrogen [4]. The host lattice is locally distorted around an occupied site, resulting in an expansion of the V layers upon absorption of hydrogen. Due to the adhesion of the sample to the substrate and
the restoring field from the Fe layers the expansion is limited to the direction perpendicular to the film. In Fe/V(001) superlattices an unusually large lattice expansion has been observed upon hydrogen uptake, which was attributed to the site occupancy of the H atoms in the V host [5]. From the size of the expansion coefficient it was inferred that the hydrogen atoms occupy only octahedral $z$ sites, sketched in Fig. 2.1. The local structure of the hydrogenated V layers has been studied in Paper I using extended x-ray absorption fine structure (EXAFS) as a local structural probe. The EXAFS technique is covered in Section 2.2.

A characteristic property of magnetic superlattices, i.e., samples that contain at least one magnetic constituent like Fe, is the interlayer exchange coupling that couples adjacent magnetic layers across the non-magnetic layers. This coupling is mediated via a polarization of the spacer layer’s conduction electrons in an RKKY-type [6] of fashion and has first been observed in Fe/Cr/Fe trilayers [7] and Gd/Y superlattices [8]. It is an oscillating function of the non-magnetic layer’s thickness $d$ with an envelope that decreases as $1/d^2$. The period of the oscillation is given by the shape of the spacer’s Fermi surface, its strength and its phase are determined by the spin-dependent reflection of the conduction electrons at the magnetic interface [9, 10]. In Fe/V(001) superlattices, e.g., for $d_V = 12, 13, 14$ ML and not too thick Fe layers an antiferromagnetic (AFM) coupling of adjacent magnetic layers is observed [11]. All other V thicknesses result in a parallel orientation of the Fe layers.

A rather unique phenomenon that is observed in Fe/V(001) superlattices is the ability to modify the interlayer exchange coupling by selective alloying of the V spacer with hydrogen. It has first been studied by Hjörvarsson et al. using neutron scattering [12]. The authors observed a reversible switching of the magnetic coupling in Fe$_3$/V$_m$(001) superlattices from initially AFM to ferromagnetic (FM) coupling for $m = 12$ and 14, as well as a switching from FM to AFM and, with further increased hydrogen concentration, back to FM for $m = 15$, upon alloying.

The ability to modify the interlayer coupling using hydrogen is exploited in Paper II, in which the realization of quasi-two-dimensional magnetism in a weakly coupled Fe/V(001) superlattice was studied. A property that is essential for studies of phase transitions is the excellent structural quality and homogeneity of the samples, which is, apart from the structural characterizations, even reflected in their magnetic properties. Ferromagnetic resonance (FMR) [13] studies revealed a very small uniaxial anisotropy induced by steps on the substrate [14], which indicates the existence of very large atomically flat terraces resulting in a perfect structural quality. The excellent magnetic homogeneity of the samples has also been confirmed by magnetic susceptibility measurements [15, 16] and is reflected in a small width of the diverging susceptibility at the paramagnetic to ferromagnetic phase transition.
8.5 9.0 9.5 10.0 10.5 11.0 11.5
E [keV]

0 1 2 3
µ(E)

µx
µ0

0 5 10 15
k [Å⁻¹]

-0.2 -0.1 0 0.1 0.2
χ(k)

0 5 10 15

Figure 2.2: K-edge X-ray absorption spectrum of a thin Cu foil at 10 K [18]. It is the wiggly part above the edge, the EXAFS $\chi(E)$, that contains the structural information about the local surrounding of the absorbing atom. The inset shows the extracted EXAFS $\chi(k)$.

2.2 EXAFS

The subject of Paper I is the determination of the local structure of the V layers in an Fe$_3$/(VH$_{0.5}$)$_{13}$ (001) superlattice by extended x-ray absorption fine structure (EXAFS) measurements, which will be presented in this section. It is based on the review given by Koningsberger [17] and the course by Bruce Ravel [18]. EXAFS is a technique that yields detailed structural information about the local surrounding of atoms of a certain species.

In EXAFS one measures the energy dependent linear absorption coefficient $\mu(E)$ of a sample. The change in intensity of an incident beam of photons with intensity $I_0$ traveling a distance $dx$ in a material with absorption coefficient $\mu$ is given by

$$dI = -\mu(E)I_0 dx,$$  

which can be integrated to give Lambert’s law,

$$I(x) = I_0 e^{-\mu(E)x}.$$  

The absorption coefficient decreases smoothly with increasing energy unless the incident photons have enough energy to excite a core electron into an unoccupied state above the Fermi level, thereby emitting a photoelectron. This process leads to a step-like increase of $\mu(E)$ at the absorption edge $E_0$. It is this feature that makes EXAFS an element-specific technique and allows one
to investigate the local structure around a certain atomic species. Depending on which shell the electron was occupying prior to the excitation, the absorption edge is denoted as $K$ edge, $L$ edge, and so forth.

If one could measure the absorption spectrum of a single atom, $\mu(E)$ would be decreasing smoothly with increasing energy after the edge, shown as $\mu_0(E)$ in Fig. 2.2. However, the experimental spectrum given as an example in Fig. 2.2 is not smooth at all. It is the wiggly part above the absorption edge, the EXAFS $\chi(E)$, that contains the structural information. It is defined as the oscillatory variation of the smooth atomic absorption coefficient $\mu_0$,

$$
\mu(E) = \mu_0(E) \left[ 1 + \chi(E) \right].
$$

(2.3)

In a heuristic picture, the photoelectron that is emitted by the absorbing atom propagates as a spherical wave, is scattered off the surrounding atoms, and interferes with the outgoing wave. The interference pattern depends on the phase shift of the backscattered wave and therefore on the path length traveled by the electron. Thus, local structural information is contained in the photoelectron’s wave function. Fig. 2.3 shows a simplistic picture of this process.

From Eq. (2.2) a simple way to experimentally determine $\mu(E)$ can be derived. The intensity $I_0$ of the incident beam and that of the transmitted beam, $I_t$, is measured as a function of energy. Then $\mu$ can be calculated from

$$
\mu_\epsilon = \ln \frac{I_0}{I_t}.
$$

(2.4)

The quantity $\mu_\epsilon$ defined here is not identical to $\mu$ in Eq. (2.2) and includes the
Figure 2.4: Results from the analysis of the Cu data, Fig. 2.2, using IFEFFIT [19, 20].
For the dotted line only the first shell has been fitted using one single-scattering path. The dashed-line fit takes into account seven paths up to the third-shell distance.

thickness of the sample as well as the detector efficiencies. The absolute value of \( \mu \) is, however, not relevant. The EXAFS \( \chi(\mu) \) is the oscillatory part of the absorption spectrum on the atomic-like background \( \mu_0(\mu) \), normalized to the jump at the absorption edge \( \mu_0(E_0) \),

\[
\chi(\mu) = \frac{\mu_\chi(\mu) - \mu_0(\mu)}{\mu_0(E_0)} .
\]  

(2.5)

As a final step, \( \chi \) is transformed from energy to \( k \) space, using the free-electron relation

\[
k = \frac{\sqrt{2m_e(h\nu - E_0)}}{\hbar}.
\]  

(2.6)

The result of this procedure, \( \chi(k) \), is plotted in the inset of Fig. 2.2. Its Fourier transform \( \chi(R) \), plotted in the upper part of Fig. 2.4, is related to the radial distribution function of the atoms surrounding the absorber. The peaks corre-
spond to the distinct shells of neighboring atoms. However, in order to extract quantitative structural information, the experimental spectra have to be analyzed by fitting them to calculated spectra that are based on a (physically reasonable) structural model. In the following the analysis of EXAFS spectra using an approach based on multiple scattering theory is outlined.

According to multiple scattering theory, $\chi(k)$ can be computed as the sum of contributions from different scattering paths $\Gamma$,

$$\chi(k) = \sum_{\Gamma} \chi_\Gamma(k). \quad (2.7)$$

The oscillatory behavior of the absorption is caused by the first exponential factor in Eq. (2.8). Its argument, the phase factor, has two contributions. The first is the phase shift $2kR_\Gamma$ due to the path traveled, where $R_\Gamma$ is the half width of the absorption edge. The second contribution is $\Phi_\Gamma(k)$, which originates from the mean path length $L_\Gamma$ and the mean square displacement $\langle \xi^2 \rangle$.

$$\chi_\Gamma(k) = \text{Im} \left( \frac{(N_\Gamma S_\Gamma^2)}{kR_\Gamma^2} e^{i(2kR_\Gamma + \Phi_\Gamma(k))} e^{-2\sigma^2 k^2} e^{-2R_\Gamma/\lambda(k)} \right). \quad (2.8)$$

Eq. (2.7) and (2.8) constitute the EXAFS equation. It is quoted here to illustrate the physical meaning of its terms and to identify some of the parameters. The oscillatory behavior of the absorption is caused by the first exponential factor in Eq. (2.8). Its argument, the phase factor, has two contributions. The first is the phase shift $2kR_\Gamma$ due to the path traveled, where $R_\Gamma$ is the half width of the absorption edge.
path length. The second is the phase shift \( \Phi_\Gamma \) due to the change in potential experienced by the electron, both at the absorber and the scatterer:

\[
\Phi_\Gamma = 2\Phi_{\text{absorber}} + \Phi_{\text{scatterer}}.
\]  

The second exponential factor in Eq. (2.8) is related to structural disorder and/or thermal motion, and the third exponential is simply the damping due to the mean-free path of the electrons. Defining \( R_{\Gamma} \equiv R_{0,\Gamma} + \Delta R_{\Gamma} \), the nominal half path length \( R_{0,\Gamma} \), the scattering amplitude \( F_{\Gamma} \), the phase shift \( \Phi_{\Gamma} \), and the mean-free path \( \lambda \) are obtained from multiple-scattering calculations based on a structural model. The parameters used as fitting variables are the change in half path length \( \Delta R_{\Gamma} \), the path multiplicity \( N_{\Gamma} \), and the mean-square displacement \( \sigma_{\Gamma} \). From these parameters the structural information (bond length, structural disorder, and coordination number) can be derived. The multiple-scattering calculations in this work were performed using FEFF7 [21, 22] and consist of three steps. First, the potentials and phase shifts are calculated. Second, all possible scattering paths within a certain cluster of atoms are calculated, taking into account the symmetry and the degeneracy of the paths. Third, the scattering amplitudes and phase shifts for each path are calculated. The importance of each path is then evaluated and less important paths are neglected.

In the next step of the analysis procedure a fitting routine is used to find the best set of parameters to fit the sum of paths (Eqs. (2.7) and (2.8)) to the experimental \( \chi(k) \). The fit is commonly performed using the Fourier transform \( \chi(R) \) and is limited to the region of interest in \( R \)-space, i.e., the region that corresponds to the shells of scatterers that are to be fitted. The number of independent fitting variables can be reduced by constraints that emerge from the structural model used to perform the fit. For the work presented in this thesis IFEFFIT [19, 20] was used for the analysis of the data. As an example, two different fits for the Cu data from Fig. 2.2 are presented in Fig. 2.4. The first fit uses only one single-scattering path and is limited to the first shell, whereas the second fit includes seven paths up to the third-shell distance. The latter fit allows to extract more structural information, e.g., by using a more complicated structural model that contains more fitting parameters. In that way one can differentiate structures that are locally similar but differ from each other if the range of data used in the fit is extended beyond the first shell.

### 2.3 Magnetism and dimensionality

Following an idea put forward by Kadanoff [23], all phase transitions can be divided into a small number of universality classes depending on the dimensionality of the system and the symmetry of the order parameter. Within each
class all physical systems undergoing a phase transition behave identically in the critical region, no matter which microscopic interaction gives rise to the transition. That is, the density during a liquid-gas phase transition shows the same critical behavior as the magnetization of a uniaxial ferromagnet at the Curie temperature. As will be discussed below, the mere presence or absence of a phase transition to a state with long-range order at non-zero temperature is crucially dependent on which universality class a particular system belongs to.

In the case of magnetic phase transitions, to which the discussion will be limited in the following, the order parameter is the spontaneous magnetization $M$. The number of its components $n$, also denoted as spin symmetry or spin dimensionality, and the (spatial) dimensionality of the system undergoing the phase transition determine its universality class. The spatial dimensionality of a system is determined by the extent (the number of dimensions $d$) to which the critical fluctuations can propagate at the phase transition. Numerous models have been suggested to describe real physical systems and to study their critical behavior. Those that are most relevant to magnetic phase transitions are the Ising, XY, and Heisenberg models, which correspond to the three possible spin symmetries, $n = 1, 2, \text{ and } 3$, respectively.

As can be seen from Table 2.1, no phase transition to magnetic long-range order exists at a finite Curie temperature $T_C$ in one dimension, whereas such a transition always appears at $T_C > 0$ in three dimensions (3D), regardless of the system’s spin symmetry. In two dimensions (2D), however, the absence or presence of a phase transition to long-range order at a finite $T_C$ is intimately related to the spin symmetry. Its existence in the 2D-Ising model has been proven by Peierls and Onsager [24, 25]. In the XY and Heisenberg models, no phase transition to long-range order at a finite temperature occurs for $d < 3$ [26, 27]. This has also been proven for the Hubbard model, which is a more adequate description in the context of itinerant magnets [28, 29].

Despite the absence of a phase transition to a state of conventional long-range order in the 2D-XY model, a Kosterlitz-Thouless (KT) phase transition to a state with so-called topological short-range order occurs at $T_{KT} > 0$ [30, 31]. The KT phase comprises bound vortex-antivortex pairs that destroy the magnetic long-range order below $T_{KT}$. In the thermodynamic limit, i.e., in an infinite system, the KT phase is a state of infinite correlation length but no spontaneous long-range order. However, the slow power-law decay of the spin-spin correlation function at low temperatures ensures a spontaneous magnetization in any finite system [32].

Two-dimensional magnets can be realized experimentally by ultra-thin magnetic films on non-magnetic substrates or by compounds of such layers.

\[ \text{For the sake of simplicity, the discussion will be limited to ferromagnets. Most of it applies also to antiferromagnets, with } T_C \text{ replaced by the Néel temperature } T_N. \]
separated by non-magnetic spacer layers, where the magnetic layers are only a few atomic layers thick. In the case of a layered magnetic system the interlayer coupling $J'$ across the non-magnetic spacer is much weaker than the intralayer coupling $J$, $J' \ll J$. For a vanishing $J'$, a multilayer would comprise an ensemble of independent 2D magnets. However, a small interlayer exchange coupling always exists and all experimental systems are therefore quasi-2D. Nevertheless, 2D-behavior might be expected if the interlayer coupling is small enough [33, 34].

The spin symmetry of an experimental magnet is imposed by its magnetic anisotropy. The last column in Table 2.1 relates the spin symmetry of the models discussed here to the magnetic anisotropy of experimental systems. The Ising model is representative of magnets with a uniaxial magnetic anisotropy, i.e., either thin films with an easy axis of magnetization perpendicular to the film, or films with an in-plane easy axis induced by a stepped substrate or by epitaxy. The Fe$_3$/V$_{m}$(001) superlattices studied in Paper II possess an easy-plane magnetization and are therefore an experimental realization of the XY model. The Heisenberg model is representative of magnetic samples with no preferred direction of the magnetization. A small anisotropy is virtually always present, either of crystalline origin with the symmetry of the underlying lattice or induced by epitaxial growth and/or stepped substrates. Thus, magnetic films with a complete isotropic behavior or an easy-plane behavior are rare.

Even though the existence of magnetic long-range order is prohibited, as described by the Mermin-Wagner theorem [26, 27], a spontaneous magnetization can be stabilized by small perturbations to the 2D-XY and 2D-Heisenberg Hamiltonians, e.g., an arbitrarily small anisotropy [35] or a non-vanishing interlayer coupling [36]. However, two-dimensional XY or Heisenberg behavior can be observed if these perturbations are minimized. Which type of critical behavior actually is observed depends on the relative size of the different con-

<table>
<thead>
<tr>
<th>spin symmetry</th>
<th>$d = 1$</th>
<th>$d = 2$</th>
<th>$d = 3$</th>
<th>magnetic anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ising</td>
<td>$n = 1$</td>
<td>⨿</td>
<td>⨿</td>
<td>uniaxial</td>
</tr>
<tr>
<td>XY</td>
<td>$n = 2$</td>
<td>⨿</td>
<td>•</td>
<td>planar</td>
</tr>
<tr>
<td>Heisenberg</td>
<td>$n = 3$</td>
<td>⨿</td>
<td>⨿</td>
<td>isotropic</td>
</tr>
</tbody>
</table>

Table 2.1: Models for magnetic phase transitions. The absence (○) or presence (●) of a phase transition to a long-range ordered state at a finite temperature is crucially dependent on the dimensionality $d$ and the spin symmetry $n$ of the system, i.e., its universality class. The last column relates the models to experimentally relevant magnetic anisotropies.
tributions to the Hamiltonian. As an example, consider the following case:

\[ H = H_0 + H_{\text{inter}} + H_{\text{Ising}} \]  

(2.10)

In Eq. (2.10) \( H_0 \) represents a perfect 2D-Heisenberg system, \( H_{\text{inter}} \) the effect of an interlayer coupling \( J' \), and \( H_{\text{Ising}} \) an Ising-like magnetic anisotropy characterized by a coefficient \( I \). We assume that the intralayer coupling is much stronger than the two perturbations that \( H_{\text{inter}} \) and \( H_{\text{Ising}} \) constitute, i.e., \( J \gg J', I \). At sufficiently high temperatures the system will therefore behave as a 2D-Heisenberg magnet. As the temperature is lowered, and \( J' > I \), the system will undergo a dimensionality crossover and behave as a 3D-Heisenberg magnet. Finally, at even lower temperatures an anisotropy crossover to a 3D-Ising magnet takes place. If \( J' < I \) however, the system will first undergo an anisotropy crossover to a 2D-Ising behavior and, at even lower temperatures, a dimensionality crossover to a 3D-Ising system. For certain ratios of the parameters \( J, J', \) and \( I \) the different types of crossovers occur in the critical region and are manifested as changes in the critical exponents.

Previous studies of the dimensionality aspects of magnetic phase transitions have been focused on intercalated transition-metal based compounds. Most of the work done has been reviewed by de Jongh [37]. There exists a whole zoo of related systems with different kinds of anisotropies and varying interlayer coupling. As an example, the series of quasi-2D Heisenberg ferromagnets \((C_nH_{2n+1}NH_3)_{2}CuCl_4 (n = 1, 2, 3, 10)\) covers a wide range of interlayer coupling constants \((J'/J = 10^{-3}–10^{-6})\) [38]. From magnetic susceptibility measurements clear evidence for a dimensional crossover at \( T_C^- \) has been found. In addition to that, spin-dimensionality crossovers have been observed and are attributed to the presence of small XY- and Ising-like anisotropies. 2D-XY like behavior has been observed in BaM\(_2\)(XO\(_4\))\(_2\) (M = Co, Ni; X = P, As) [34], K\(_2\)CuF\(_4\) [39], and NiCl\(_2\)- and CoCl\(_2\)-graphite intercalated compounds [40]. The usefulness of these “classical” systems is limited by structural imperfections that hinder the divergence of the critical fluctuations at the phase transitions. The extension of crystallographically well correlated magnetic sheets in the film plane is far from infinite. Since the advent of modern UHV growth techniques like molecular-beam epitaxy and sputter deposition, metallic magnetic samples with a superior in-plane structural correlation length can be grown. Many of the systems that have been investigated grow epitaxially in a layer-by-layer mode, resulting in thin films or layered samples with a low defect density and an in-plane correlation length only limited by substrate-induced steps. The Fe/V(001) superlattices presented in Section 2.1 are an example of such a system, both in terms of structural coherence and magnetic homogeneity.

The critical behavior of magnetic phase transitions is commonly discussed in terms of critical exponents that describe the behavior of a function \( f(\varepsilon) \)
near the critical temperature, which—for the sake of simplicity—is assumed to be the Curie temperature $T_C$. The dimensionless variable

$$\varepsilon \equiv \frac{T - T_C}{T_C}$$

measures the difference in temperature from $T_C$. For sufficiently small, positive values of $\varepsilon$, the critical exponent $\lambda$ is defined as the limit

$$\lambda \equiv \lim_{\varepsilon \to 0} \frac{\ln f(\varepsilon)}{\ln \varepsilon}.$$  

The most frequently used quantities in the discussion of magnetic phase transitions are the zero-field magnetization $M$ and the zero-field magnetic susceptibility

$$\chi \equiv \frac{\partial M(H)}{\partial H} \bigg|_{H=0},$$

where $H$ is the applied magnetic field. Their respective critical behavior follows a power-law,

$$M \propto (-\varepsilon)^\beta, \quad \varepsilon \leq 0,$$

$$\chi \propto \varepsilon^{-\gamma}, \quad \varepsilon \geq 0,$$

where $\beta$ and $\gamma$ are the critical exponents. Critical exponents belonging to the same phase transition are related by scaling laws and are characteristic of the corresponding universality class. Thus, the universality class of a particular physical system or phase transition can be determined by measuring one (or preferably several) of its critical exponents. In Table 2.2 theoretical values of the critical exponents $\beta$ and $\gamma$ are presented for $d = 2$ and 3. The value for the 2D-XY model has been calculated by a renormalization method and is characteristic for a system of finite size [32].

Bramwell and Holdsworth did a survey of published critical exponents $\beta$ of the layered classical compounds discussed above [44]. They found that

<table>
<thead>
<tr>
<th>spin symmetry</th>
<th>$d = 2$</th>
<th>$d = 3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ising</td>
<td>$n = 1$</td>
<td>0.125</td>
</tr>
<tr>
<td>XY</td>
<td>$n = 2$</td>
<td>0.23</td>
</tr>
<tr>
<td>Heisenberg</td>
<td>$n = 3$</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.2: Theoretical values for the 2D and 3D critical exponents $\beta$ and $\gamma$ defined in Eq. (2.14) [41]. The 2D-XY value $\beta \approx 0.23$ is a result for a finite-size system [32].
most of them fall into one of two universality classes, those of the 2D-Ising model and the finite-size 2D-XY model. Systems with critical exponents different from these either exhibit a very weak Ising-like anisotropy and are intermediate between 2D-Ising and 2D-XY, or possess a rather strong interlayer coupling and are therefore intermediate between 2D and 3D. A more recent survey of the critical behavior of metallic thin films and multilayers can be found in Ref. [45].

2.4 MOKE

The magnetic susceptibility and magnetization measurements presented in Paper II are based on the magneto-optical Kerr effect (MOKE), which was discovered by John Kerr in 1877. After the first MOKE experiments on ultra-thin magnetic films have been reported about 20 years ago [46], this technique has become a common tool in the field of thin film magnetism and has even found an industrial application in magneto-optical data storage [47]. The advantages of MOKE as a tool for magnetometry are its monolayer sensitivity and the relatively simple experimental setup. It is usually performed in air but has also been implemented as an in-situ technique attached to UHV growth systems. An excellent review on the technique and the fields of research that emerged from it has been recently given by Qiu and Bader [48].

The microscopic origin of the magneto-optical effects is the interaction between the light passing through or reflecting from a medium and the electrons’ orbital degrees of freedom, which, in turn, are coupled to the spin via the spin-orbit coupling. The magneto-optical response of a medium is two-fold: one is the rotation of the polarization of light due to the phase shift caused by the different velocities of light in the medium, and the second is the change in ellipticity caused by the difference in absorption. In optical terms, the magneto-optical effects constitute a birefringence induced by the magnetization of the medium.

A simple MOKE experiment is sketched in Fig. 2.6. It consists of a polarized light source, usually a laser and a polarizer, and—after reflection of the light by the sample that is subject to a magnetic field—an analyzer and a detector. The situation shown here, with the magnetization in the plane of the film and in the plane of incidence, is denoted the longitudinal configuration. In the transverse configuration the magnetization is in the film plane but perpendicular to the plane of incidence. Its Kerr effect only gives rise to a

The Faraday (transmission) and Kerr (reflection) effects are linear in the applied magnetic field, whereas the Voigt effect (transmission) is quadratic. The latter differs also from the Faraday effect in that the magnetization is perpendicular to the propagation of light in the medium. Due to the strong absorption of light in metals the Kerr effect is almost exclusively used.
change in intensity of the reflected light and is more difficult to detect. The polar configuration measures a magnetization perpendicular to the film plane. Its signal is about one order of magnitude larger than that of the longitudinal Kerr effect and is employed in magneto-optical recording [47].

In most cases MOKE is used to record hysteresis loops, i.e., the total magnetization of a sample is measured as a function of an applied field at a fixed wavelength of light. Both the Kerr rotation and the ellipticity are proportional to the sample’s magnetization so that either of them can be measured. The information that is obtained in a MOKE experiment is the integrated magnetization of the sample within the spot size of the light, weighted by the magneto-optical response of the specific materials and the attenuated intensity of light at the specific depth. The probing depth is of the order of the wavelength of the light used, i.e., typically several 100 nm. MOKE can easily be adapted to measure the magnetic susceptibility $\chi$ defined in Eq. (2.13), if the sample is placed in the center of a pair of Helmholtz coils which supply a small oscillating magnetic field. The Kerr signal is detected by a lock-in amplifier, which output is directly proportional to $\chi$. This technique is frequently denoted as ac-MOKE.

2.5 Summary of Papers I and II

In Paper I the changes of the local structure of the V layers in an Fe$_3$/V$_{13}$(001) superlattice upon alloying with hydrogen were studied using EXAFS. Going from V to VH$_{0.5}$ the initial bct structure is strongly distorted and resembles the local structure of bulk $\beta$-V-hydride. The expansion of the out-of-plane lattice parameter was determined to be 7.3%. The average expansion of the entire V layer—taking into account the hydrogen-depleted interface regions—amounts
to 5.1% and is in agreement with previous results from XRD.

The effect of hydrogen on the interlayer exchange coupling in an identical sample, which is in a regime of weak coupling, was studied in Paper II. A phase with short-range magnetic order was observed in a wide temperature range between the paramagnetic phase and the onset of long-range order. It is interpreted as two-dimensional-XY behavior and is attributed to the absence of a magnetic anisotropy within the magnetic layers and the vanishing of the interlayer exchange coupling close to the ordering temperature.
3. Electronic structure calculations

3.1 Introduction

The subject of this chapter is electronic structure calculations, which form the basis of Papers III to IX. It is largely based on the books by Martin [49] and Skriver [50]. The objective of this type of calculations is to study the properties of materials from first principles, i.e., only with the atomic number of the constituent atoms as an input, without any adjustable parameters. In practice, experimental information is frequently used, such as the crystal structure of the material under investigation.

First, the physical problem will be stated, which is that of many interacting electrons in an external potential. Density functional theory, which is presented in Section 3.3, reduces the complexity of the problem by expressing it as a function of the electron density only. In the next step, the Kohn-Sham approach introduced in Section 3.4, the many-body problem is replaced by an independent-particle problem that has to be solved iteratively until self-consistency is reached, with all complicated many-body interactions collected in an exchange-correlation functional, for which working approximations exist (Section 3.5). In Section 3.6 the iterative procedure used to solve the Kohn-Sham equations is outlined. Finally, after stating the Bloch theorem for crystals in Section 3.7, the computational approach of linear muffin-tin orbitals is presented in Section 3.8. The chapter closes with a short discussion of full-potential methods and relativistic effects in Sections 3.9 and 3.10.

3.2 The many-electron problem

A crystal is composed of electrons and nuclei, where the latter are arranged periodically in space. Such a system of many interacting electrons and nuclei is described by the following Hamiltonian, in which, for simplicity, relativistic effects are neglected:

$$
\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_i \frac{Z_i e^2}{|r_i - R_i|} - \sum_f \frac{Z_f e^2}{|R_f - R_j|} + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_f e^2}{|R_f - R_j|},
$$

(3.1)
where all electron coordinates and subscripts are lower case letters, whereas those of the nuclei are denoted by capitals. The first and fourth term of the Hamiltonian are the kinetic energy of the electrons and the nuclei, respectively. The second, third, and fifth term are the electrostatic Coulomb interaction among the electrons, between the electrons and the nuclei, and among the nuclei, respectively. This Hamiltonian is too complicated to be used for real systems with many electrons, and a great part of electronic structure theory is to find approximations to Eq. (3.1) that make the problem feasible to solve, without losing to much of the physics of the original problem. The most difficult part is the second term of the Hamiltonian, which describes the interaction between the electrons.

As a first approximation, the mass of the nuclei, \( M_i \), is set to infinity, so that the fourth term is eliminated from Eq. (3.1). This so-called Born-Oppenheimer approximation is justified by the fact the the mass of the nuclei is much larger than that of the electrons. Since the nuclear motion is much slower than that of the electrons, the nuclei can to a good approximation be considered to be fixed at their positions, so that the fourth term in Eq. (3.1) vanishes. The last term in Eq. (3.1) is the classical mutual electrostatic interaction of the ions. Since it is not intrinsic to the many-electron problem it will be excluded from the following discussion, but has to be considered if the total energy of a system of electrons and nuclei is to be calculated. Thus, we are left with three terms in the Hamiltonian:

\[
\hat{H} = \hat{T} + \hat{V}_{\text{e-e}} + \hat{V}_{\text{ext}}.
\]  

(3.2)

In the following, Rydberg atomic units will be adopted, \( \hbar = 2m_e = e^2/2 = 1 \), and the different terms of Eq. (3.2) are

\[
\begin{align*}
\hat{T} &= -\sum_i \nabla_i^2 \\
\hat{V}_{\text{e-e}} &= \sum_{i \neq j} \frac{1}{|r_i - r_j|} \\
\hat{V}_{\text{ext}} &= \sum_i V_i(|r_i - R_i|).
\end{align*}
\]

(3.3)

The first term, \( \hat{T} \), is the kinetic energy of the electrons, \( \hat{V}_{\text{e-e}} \) is the electron-electron interaction, and \( \hat{V}_{\text{ext}} \) is the potential acting on the electrons due to the nuclei or, more general, the ions. This form of \( \hat{V}_{\text{ext}} \) in Eq. (3.3) is more general than in Eq. (3.1) and includes pseudopotentials that take into account the effect of the core electrons. Even terms due to electrical or magnetic fields can be included here.

The next step is to calculate the expectation value of the Hamiltonian, Eq. (3.2), which is the total energy of the system of interacting particles. The
expectation value of any operator \( \hat{O} \) of a system described by the Hamiltonian \( \hat{H} \) can be calculated from
\[
\langle \hat{O} \rangle = \frac{\langle \Psi | \hat{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle},
\]
(3.4)

where the many-body wavefunction \( |\Psi\rangle \equiv \Psi(\{r_i\}) \) is an eigenstate of the time-independent Schrödinger equation
\[
\hat{H} |\Psi\rangle = E |\Psi\rangle,
\]
(3.5)

which is the fundamental equation governing a non-relativistic quantum system of interacting particles. Specifically, the energy can be calculated as the expectation value of the Hamiltonian,
\[
E \equiv \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{\text{e-e}} \rangle + \int d^3r V_{\text{ext}}(r)n(r),
\]
(3.6)

where the charge density \( n(r) \) is calculated as the expectation value of the density operator
\[
\hat{n}(r) = \sum_{i=1}^{N} \delta(r - r_i).
\]
(3.7)

According to the Rayleigh-Ritz principle the eigenstates of Eq. (3.5) make the expression for the energy, Eq. (3.6), stationary. The ground state wavefunction \( |\Psi_0\rangle \) yields the lowest energy and can in principle be determined by minimizing Eq. (3.6) with respect to \( |\Psi\rangle \). Excited states are saddle points of the energy with respect to variations in \( |\Psi\rangle \).

It is instructive to rewrite the expression for the total energy, Eq. (3.6), and separate out the energies that are due to the classical long-range Coulomb interaction,
\[
E_{\text{Coulomb}} = E_{\text{Hartree}} + \int d^3r V_{\text{ext}}(r)n(r),
\]
(3.8)

where \( E_{\text{Hartree}} \) is the electrostatic interaction of a classical charge density \( n(r) \),
\[
E_{\text{Hartree}} = \frac{1}{2} \int d^3r d^3r' \frac{n(r)n(r')}{|r - r'|}.
\]
(3.9)

Now, the total energy, Eq. (3.6), can be written as
\[
E = \langle \hat{T} \rangle + (\langle \hat{V}_{\text{e-e}} \rangle - E_{\text{Hartree}}) + E_{\text{Coulomb}}.
\]
(3.10)

The second term, contained in brackets, is the difference between the Coulomb energy of interacting correlated electrons with density \( n(r) \) and that of a continuous classical charge distribution with the same density. All
long-range effects cancel in the difference, so that the effects of this term, which is the potential part of the exchange-correlation energy in density functional theory, are short ranged.

The full many-body Schrödinger equation involves $3N$ degrees of freedom for a system of $N$ electrons and can only be solved for very small systems. The achievement of density functional theory is to cast the problem into a simpler one that involves an equation for the electron density instead.

### 3.3 Density functional theory

Density functional theory (DFT) is a general theory of correlated many-body systems, but will be discussed here only in the context of interacting electrons subject to an external potential due to fixed nuclei, as described by the Hamiltonian in Eq. (3.2). The fundamental principle of DFT, as put forward by Hohenberg and Kohn in 1964 [51], is that any property of a system of many interacting particles can be expressed as a functional of the ground state density $n_0(r)$. However, nothing is said about how to construct these functionals. The fact that DFT today is the primary tool for electronic structure calculations is due to the approach by Kohn and Sham, discussed in the next section, which has provided a way to make useful approximate ground state functionals for real many-electron systems. In this section the two theorems that are the basis of DFT are stated, together with some implications. The proofs are in fact simple and can be found in numerous texts on DFT, e. g., Ref. [49].

**Theorem I** For any system of interacting particles in an external potential $V_{\text{ext}}(r)$, the potential $V_{\text{ext}}(r)$ is determined uniquely, except for a constant, by the ground state particle density $n_0(r)$.

**Theorem II** A *universal* functional$^1$ for the energy $E[n]$ in terms of the particle density $n(r)$ can be defined, valid for any external potential $V_{\text{ext}}(r)$. For any particular $V_{\text{ext}}(r)$, the exact ground state energy of the system is the global minimum value of this functional, and the density that minimizes the functional is the exact ground state density $n_0(r)$.

From Theorem I it follows that the Hamiltonian is fully determined, except for a constant shift of the energy, and with it the many-body wavefunction for all states (ground and excited states). Hence, all properties of the system are completely determined by the ground state density. An implication of Theorem II is that the functional $E[n]$ alone is sufficient to determine the exact ground state density.

$^1$The term *universal* means the same for all electron systems.
Since all the properties such as the kinetic energy, interaction energies, etc., are uniquely determined if \( n(r) \) is given, then each such property can be expressed as a functional of \( n(r) \). Thus, the expression for the energy, Eq. (3.6), can be written as

\[
E_{HK}[n] = T[n] + E_{e-e}[n] + \int d^3r V_{ext}(r)n(r)
\]

\( \equiv F_{HK}[n] + \int d^3r V_{ext}(r)n(r) \).

(3.11)

The functional \( F_{HK}[n] \equiv T[n] + E_{e-e}[n] \) includes all internal energies of the interacting electron system and is universal by construction, since the kinetic energy and the interaction energy of the electrons are functionals of the density only and independent of \( V_{ext}(r) \). Thus, if the universal functional \( F_{HK}[n] \) was known, one could find the exact ground state density end energy by minimizing \( E_{HK}[n] \) with respect to variations in the density. It is the subject of the next section how to construct approximate functionals for real electron systems.

### 3.4 The Kohn-Sham approach

The approach suggested by Kohn and Sham in 1965 [52] turned DFT into a useful tool and is nowadays the basis of most electronic structure calculations. The idea of Kohn and Sham was to replace the original many-body problem by an independent-particle problem with all the complicated many-body interactions incorporated into an exchange-correlation functional \( E_{xc}[n] \) of the density \( n(r) \). The ground state density \( n_0(r) \), which has to be determined self-consistently, is required to be equal to that of the original interacting system. Thus, by solving the independent-particle equations one finds the ground state density and energy of the original interacting system with the accuracy only limited by the approximations in the exchange-correlation functional \( E_{xc}[n] \).

The system of independent particles that replaces the original interacting system is chosen to be described the Hamiltonian

\[
\hat{H}_{KS}^\sigma = -\nabla^2 + V_{KS}^\sigma(r),
\]

(3.12)

with the usual kinetic energy operator and an effective local potential \( V_{KS}^\sigma(r) \) that may be spin dependent\(^2\) but otherwise not specified. For a system of \( N = N^\uparrow + N^\downarrow \) independent electrons obeying this Hamiltonian the ground state has one electron in each of the \( N^\sigma \) orbitals \( \psi_i^\sigma \) which are eigenfunctions of

\[
\hat{H}_{KS}^\sigma \psi_i^\sigma = \epsilon_i^\sigma \psi_i^\sigma
\]

(3.13)

\(^2\)Note that the external potential \( V_{ext}(r) \) due to the ions is still spin independent.
with the lowest eigenvalues \( \epsilon^\sigma_i \). The density is then calculated from

\[
n(r) = \sum_\sigma n^\sigma(r) = \sum_\sigma \sum_{i=1}^{N^\sigma} |\psi^\sigma_i(r)|^2, \tag{3.14}
\]

and the independent-electron kinetic energy \( \hat{T}_s \) is given by

\[
\hat{T}_s = -\sum_\sigma \sum_{i=1}^{N^\sigma} \langle \psi^\sigma_i | \nabla^2 | \psi^\sigma_i \rangle = \sum_\sigma \sum_{i=1}^{N^\sigma} |\nabla \psi^\sigma_i|^2. \tag{3.15}
\]

The crucial step of the Kohn-Sham approach is to rewrite the Hohenberg-Kohn functional for the ground state energy, \( E_{HK} \) (Eq. (3.11)):

\[
E_{KS}[n] = T_s[n] + \int d^3r V_{\text{ext}}(r)n(r) + E_{\text{Hartree}}[n] + E_{xc}[n]. \tag{3.16}
\]

In the Kohn-Sham approach, all many-body effects of exchange and correlation are grouped into the exchange-correlation energy functional \( E_{xc}[n] \). Comparing \( E_{KS}[n] \) and \( E_{HK}[n] \), Eqs. (3.11) and (3.16), \( E_{xc}[n] \) can be written as

\[
E_{xc}[n] = E_{HK}[n] - (T_s[n] + E_{\text{Hartree}}[n]) = \left( \langle \hat{T} \rangle - T_s[n] \right) + \left( \langle \hat{V}_{\text{e-e}} \rangle - E_{\text{Hartree}}[n] \right). \tag{3.17}
\]

Thus, the exchange-correlation energy \( E_{xc} \) is just the difference of the kinetic and the interaction energies of the original interacting many-body system from those of the chosen independent-particle system, with the real electron-electron interaction replaced by the Hartree energy. Minimization of \( E_{KS}[n] \) with respect to variations of the electron density leads to the Schrödinger-like Kohn-Sham equations (3.13) with the effective Kohn-Sham Hamiltonian \( \hat{H}_{KS}^\sigma \), Eq. (3.12), where the effective potential is given by

\[
V_{KS}^\sigma(r) = V_{\text{ext}}(r) + \delta E_{\text{Hartree}}[n]/\delta n(r, \sigma) + \delta E_{xc}[n]/\delta n(r, \sigma) = V_{\text{ext}}(r) + V_{\text{Hartree}}(r) + V_{xc}^\sigma(r). \tag{3.18}
\]

The Kohn-Sham equations (3.12), (3.13), and (3.18) are independent-particle equations with a potential that has to be found self-consistently. If the exchange-correlation functional \( E_{xc}[n] \) would be known exactly, these equations would yield the exact ground state energy and density.

By separating out the independent-particle kinetic energy and the long-range Hartree term in Eq. (3.17), the remaining exchange-correlation functional \( E_{xc}[n] \) can be reasonably approximated as a local functional, and can therefore be expressed in the form

\[
E_{xc}[n] = \int d^3r n(r) \epsilon_{xc}([n], r), \tag{3.19}
\]
where $\varepsilon_{xc}(\{n\}, r)$ is the energy per electron at $r$ that depends only on the density $n(r, \sigma)$ in some neighborhood of $r$. Note that only the total density $n(r)$ appears in Eq. (3.19), all the spin information is incorporated in $\varepsilon_{xc}(\{n\}, r)$. The exchange-correlation potential $V^\sigma_{xc}(r)$, defined in Eq. (3.18), is the functional derivative of $E_{xc}[n]$ and can be written as

$$V^\sigma_{xc}(r) = \varepsilon_{xc}(\{n\}, r) + n(r) \frac{\delta \varepsilon_{xc}(\{n\}, r)}{\delta n(r, \sigma)}.$$  (3.20)

### 3.5 Exchange-correlation functionals

The method advised by Kohn and Sham consists of two important steps, i.e., to replace the original many-body problem by an independent-particle problem that is required to have the same ground state density, and to incorporate all complicated many-body interaction terms into the exchange-correlation functional $E_{xc}[n]$, Eq. (3.17). The existence of approximate functionals for $E_{xc}[n]$ derived for realistic electron systems is the basis for the success of DFT in modern electronic structure calculations.

The physical origin of exchange is the Pauli exclusion principle that forbids electrons that have the same spin to be at the same place. The effect is to reduce the repulsive Coulomb interaction, which can be expressed as the interaction of an electron with a positive exchange hole surrounding it. For the homogenous electron gas the exchange hole can be calculated analytically. The origin of correlation is screening, i.e., the collective motion of the particles to reduce the net interaction among any two particles, an effect that changes the shape of the exchange hole. In the ground state the potential energy is lowered due to correlation, whereas the kinetic energy is increased as the electrons correlate to lower their potential energy. Correlation is much more important for electrons with antiparallel spins, since those with parallel spins are kept apart by the Pauli principle.

Already Kohn and Sham pointed out that many solids can be considered as close to the limit of the homogenous electron gas, in which the effects of exchange and correlation are local [52]. In the local density approximation (LDA), the exchange-correlation energy is simply an integral over all space with the exchange-correlation energy density at each point assumed to be the same as in the homogenous electron gas with that density.

$$E_{xc}^{\text{LDA}}[n^\uparrow, n^\downarrow] = \int d^3r n(r) \varepsilon_{xc}^{\text{hom}}([n^\uparrow, n^\downarrow], r).$$  (3.21)

The exchange-correlation energy density $\varepsilon_{xc}^{\text{hom}}([n^\uparrow, n^\downarrow], r)$ can be calculated as a potential energy due to the exchange-correlation hole introduced above, averaged over the coupling strength. This is accomplished by varying the elec-
tronic charge from zero to its actual value, with the constraint that the density is kept constant. In the case of zero coupling the exchange-correlation hole is equal to the exchange hole of the homogenous electron gas and can be calculated analytically. At full coupling the exchange-correlation hole can be calculated by quantum Monte Carlo methods. Since the electron density is required to remain constant while the coupling strength is varied, $\varepsilon_{\text{xc}}^{\text{hom}}([n^\uparrow,n^\downarrow], \mathbf{r})$ is implicitly a functional of the density. Thus, $E_{\text{xc}}^{\text{LDA}}[n^\uparrow,n^\downarrow]$ can be considered as an interpolation between the exchange-only and the full correlated energies at a given density, i.e., between low- and high-density limits, respectively.

A justification of the local approximation is that for densities typically encountered in solids, the effects of exchange and correlation are rather short ranged. Furthermore, it turns out that only the spherically averaged part of the exchange-correlation hole contributes to $E_{\text{xc}}^{\text{LDA}}[n^\uparrow,n^\downarrow]$, because the Coulomb interaction between the electrons depends only on their distance $|\mathbf{r} - \mathbf{r}'|$. It is thus sufficient that the LDA provides a reasonable approximation for the spherical average of the exchange-correlation hole, something which has been verified explicitly for some cases [54].

The first step to improve on the local approximation is a functional of the magnitude of the density gradient, $|\nabla n^\sigma(\mathbf{r})|$, in addition to the value of the density $n^\sigma(\mathbf{r})$ at each point. Such a gradient expansion approximation (GEA) was already suggested by Kohn and Sham [52]. It does, however, not lead to a general improvement over the LDA, mainly because it violates a sum rule for the exchange-correlation hole, which requires that the integral of the hole over the whole space is equal to $-1$. A number of generalized gradient approximations (GGA) have been suggested that remedy this problem and correctly take into account the large gradients frequently observed in solids. These functionals are defined as a generalization of the LDA functional, Eq. (3.21),

$$E_{\text{xc}}^{\text{GGA}}[n^\uparrow,n^\downarrow] = \int d^3 r n(\mathbf{r}) \varepsilon_{\text{xc}}^{\text{hom}}([n^\uparrow,n^\downarrow],|\nabla n^\uparrow(\mathbf{r})|,|\nabla n^\downarrow(\mathbf{r})|,\ldots,\mathbf{r}).$$

(3.22)

The different GGA functionals that are in use today yield more or less the same exchange-correlation energy within a range of gradients encountered in real solids, but differ at larger gradients due to the different physical conditions chosen for the limit of infinite gradients. In general, the GGA leads to a reduction of the binding energies, correcting for the LDA overbinding and improving the agreement with experiment.

### 3.6 Solving the Kohn-Sham equations

The Kohn-Sham method provides a framework to find the exact ground state energy and density of a system of interacting electrons by using standard
independent-particle methods. The set of coupled Kohn-Sham equations has to be solved by a procedure that iteratively changes \( V_{KS}^\sigma (\mathbf{r}) \) or \( n(\mathbf{r}) \) to approach a self-consistent solution. The outline of this procedure is as follows:

1. An initial guess for the electron density is constructed, usually from an atomic calculation.
2. The effective potential, Eq. (3.18), is calculated. The Coulomb part of the potential can be calculated from the input density through the Poisson equation,

\[
\nabla^2 V_{\text{Hartree}}(\mathbf{r}) = -8\pi n(\mathbf{r}).
\]  

(3.23)

3. The Kohn-Sham equations, Eq. (3.13), are solved.
4. The electron density is calculated from Eq. (3.14)
5. If self-consistency is reached, the total energy and other quantities of interest are calculated, otherwise the procedure is continued, starting with an updated charge density at the second step.

The computationally demanding procedure is the third step, solving the Kohn-Sham equations, for which a variety of different methods have been designed. In the Section 3.8 the linear muffin-tin orbital method (LMTO) will be presented, which is the basis for the code used throughout this work.

3.7 The Bloch theorem

So far nothing was said about the arrangement of the ions that give rise to the external potential \( V_{\text{ext}}(\mathbf{r}) \) acting on the electrons. In the remainder of this chapter the discussion will be limited to crystals, i.e., structures in which the positions of all atoms, and, consequently, all physical properties, are repeated periodically in space. A crystal is completely specified by the types and positions of the atoms in one repeat unit, the unit cell, and the rules that describe the translations that, applied to the unit cell, render the complete crystal. The positions and the types of the atoms in the unit cell is the basis, and the lattice of points created by the set of translations \( \{ \mathbf{R} \} \) is the Bravais lattice. The translation vectors \( \mathbf{R} \) of a crystal are given by

\[
\mathbf{R} = \sum_{i=1}^{3} n_i \mathbf{a}_i,
\]  

(3.24)

where the vectors \( \mathbf{a}_i \) are the basis vectors that span the unit cell and the \( n_i \) are integers.

For the proof of the Bloch theorem it is convenient to define a translational operator \( \hat{T}_\mathbf{R} \) with the property

\[
\hat{T}_\mathbf{R} \psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R}).
\]  

(3.25)
Since the effective potential in the Hamiltonian has the periodicity of the crystal lattice, the Hamiltonian is invariant to translations and therefore commutes with $\hat{T}_R$,

$$\hat{H}\hat{T}_R = \hat{T}_R\hat{H}. \quad (3.26)$$

Thus, the eigenstates of $\hat{H}$ can be chosen to be eigenstates of all $\hat{T}_R$. Since the consecutive application of the translation operator is again a translation,

$$\hat{T}_R_1\hat{T}_R_2 = \hat{T}_R_{R_1+R_2}, \quad (3.27)$$

it follows that the eigenvalues $t_R$ of $\hat{T}_R$ obey the relation

$$\hat{T}_R\psi(r) = t_R\psi(r) = t_R\psi(r). \quad (3.28)$$

Each translation $t_R$ can be written as a product of primitive translations $t_a$,

$$t_R = \sum_{i=1}^{3} (t_a)^{n_i}. \quad (3.29)$$

Since the modulus of each $t_a$ must be unity it can be written as a phase factor. Hence, the eigenvalues $t_R$ can be expressed as

$$t_R = e^{ik\cdot R}, \quad (3.30)$$

where $k$ is a wavevector in reciprocal space,

$$k = \sum_{i=1}^{3} x_i b_i, \quad (3.31)$$

and the $b_i$ are the reciprocal lattice vectors defined by

$$a_i \cdot b_j = 2\pi \delta_{ij}, \quad (3.32)$$

which render the reciprocal lattice:

$$G = \sum_{i=1}^{3} m_i b_i, \quad m_i = \text{integer}. \quad (3.33)$$

From Eq. (3.30) it follows that the eigenstates of the translation operator, which are simultaneously eigenstates of the Hamiltonian as well as any other periodic operator, vary from one cell of the crystal to another only by a phase factor,

$$\hat{T}_R\psi(r) = \psi(r + R) = e^{ik\cdot R}\psi(r). \quad (3.34)$$

This is a formulation of the Bloch theorem. From Eq. (3.34) it follows that
the eigenfunctions classified by $k$ can also be written as
\[ \psi_k(r) = e^{ik \cdot r} u_k(r), \] (3.35)
where $u_k(r)$ has the periodicity of the crystal, $u_k(r + R) = u_k(r)$, since
\[ \psi_k(r + R) = e^{ik \cdot (r + R)} u_k(r + R) = e^{ik \cdot R} e^{ik \cdot r} u_k(r) = e^{ik \cdot R} \psi_k(r). \] (3.36)

So far nothing was said about the possible values for the $x_i$ in Eq. (3.31). By using a boundary condition it can be shown that the wave vector $k$ must be real and is restricted to certain allowed values. To accomplish this we assume that the crystal is composed of $N = N_1 \times N_2 \times N_3$ unit cells, and that it is repeated periodically in space, i.e.,
\[ \psi(r + N_i a_i) = \psi(r), \quad i = 1, 2, 3, \] (3.37)
which requires that
\[ e^{N_i k \cdot a_i} = 1, \quad i = 1, 2, 3. \] (3.38)

If $k$ is of the form (3.31), it follows from Eq. (3.32) that $N_i x_i$ must be an integer, and consequently
\[ x_i = \frac{n'_i}{N_i}, \quad n'_i = \text{integer}. \] (3.39)

Thus, the allowed values for the Bloch wave vectors are given by
\[ k = \sum_{i=1}^3 \frac{n'_i}{N_i} b_i, \quad n'_i = \text{integer}, \] (3.40)
with the $b_i$ defined by Eq. (3.32). The range of $k$ can be restricted to one unit cell of the reciprocal lattice, which is defined by Eq. (3.33), the so-called first Brillouin zone, since
\[ t_R = e^{i(k + G) \cdot R} = e^{ik \cdot R} e^{iG \cdot R} \] (3.41)
and $\exp(iG \cdot R) = 1$. Therefore, $n'_i = 1 \ldots N_i$, as in Eq. (3.24), and there are $N$ allowed values of $k$, one for each unit cell of the crystal.

Many properties of a crystal are calculated as a sum over the eigenstates labeled by $k$. For a function $f(k)$ the value per cell is
\[ \bar{f} = \frac{1}{N_{\text{cell}}} \sum_k f(k). \] (3.42)

For an infinite crystal, $N_{\text{cell}} \to \infty$, and $k$ becomes a continuous variable. The
sum in Eq. (3.42) converts to an integral over the Brillouin zone,

\[ \bar{f} = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d^3k \, f(k), \tag{3.43} \]

where \( \Omega_{BZ} \) is the volume of the Brillouin zone. In practice, \( \bar{f} \) is evaluated by sampling the Brillouin zone with a set of \( k \) values [55, 56] chosen such that \( \bar{f} \) is converged to sufficient accuracy.

### 3.8 The LMTO method
#### 3.8.1 Augmentation and muffin-tin orbitals

The linear muffin-tin orbital (LMTO) method is, as most of the electronic structure methods that are in use today, based on the concept of augmentation introduced by Slater in 1937 [57]. Augmented methods employ a basis set that is adapted to the physical situation encountered in solids: the potential in the vicinity of the ions resembles that of an atom, whereas it is almost constant in the region between the ions. This distinction is reflected in the so-called muffin-tin geometry in which the crystal space is divided into spheres centered around the ions, the muffin-tin spheres, and the interstitial region in-between the spheres. Often the potential is approximated as spherical inside the muffin-tin spheres of radius \( S \) and constant in the interstitial region:

\[ V_{MT}(r) = \begin{cases} V(r), & r \leq S \\ V_0, & r > S. \end{cases} \tag{3.44} \]

This is the so-called muffin-tin potential. It has the advantage that the wavefunction can be represented in terms of basis functions that are eigenfunctions in the respective region, i.e., spherical harmonics times a radial function in the muffin-tin spheres, and plane waves or other smooth functions in the interstitial region. Different methods based on augmentation have been advised, which employ different types of basis functions. In the following the LMTO method will be described, which is suitable for close-packed structures.

Muffin-tin orbitals form a basis of localized augmented orbitals. They were introduced by Andersen in 1971 [58] to allow an interpretation of the electronic structure of materials in terms of a minimal basis of physically meaningful orbitals, just like other local orbital methods. The advantage of the muffin-tin orbitals over most other local orbital methods is that they are generated from the Kohn-Sham Hamiltonian, i.e., using the actual potential, and give therefore a more accurate description of the problem.

\[ \text{To simplify the notation the presentation is limited to only one atom, i.e., one sphere, in the unit cell.} \]
The objective is to construct a solution to the Schrödinger equation with the muffin-tin potential (3.44),

\[
(\nabla^2 + V_{MT}(\mathbf{r}) - \varepsilon) \psi_L(\varepsilon, \mathbf{r}) = 0,
\]

(3.45)

where \( L = \{l, m\} \). For the chosen potential, \( \psi_L(\varepsilon, \mathbf{r}) \) can be decomposed into spherical harmonics \( Y_L \times \) a radial function,

\[
\psi_L(\varepsilon, \mathbf{r}) = i^l Y_L(\hat{r}) \psi_l(\varepsilon, r),
\]

(3.46)

where \( \hat{r} = \{\theta, \phi\} \). In the muffin-tin spheres, \( \psi_l(\varepsilon, r) \) is a solution of the radial Schrödinger equation

\[
\left( -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - \varepsilon \right) r \psi_l(\varepsilon, r) = 0.
\]

(3.47)

In the interstitial region, the solutions of Eq. (3.45) are spherical harmonics times spherical waves with a free-electron wavenumber \( \kappa \),

\[
\kappa^2 = \varepsilon - V_0.
\]

(3.48)

The spherical waves are solutions to the radial equation

\[
\left( -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \kappa^2 \right) r j_l(\kappa r) = 0.
\]

(3.49)

This is the Helmholtz equation, which has two linearly independent solutions that are labeled \( j_l(\kappa r) \) and \( n_l(\kappa r) \), the spherical Bessel and Neumann functions, respectively. If \( \kappa^2 \) is negative, the spherical Neumann function is replaced by \( -ih^{(1)}_l = n_l - ij_l \), where \( h^{(1)}_l \) is a Hankel function of the first kind.

The muffin-tin orbital is defined as a localized basis function continuous in value and derivative at the sphere boundary:

\[
\chi^\text{MTO}_L(\varepsilon, \kappa, \mathbf{r}) = i^l Y_L(\hat{r}) \left\{ \begin{array}{ll}
\psi_l(\varepsilon, r) + \kappa \cot(\eta_l) j_l(\kappa r), & r \leq S \\
\kappa n_l(\kappa r), & r \geq S,
\end{array} \right.
\]

(3.50)

which is regular everywhere in space. The matching conditions are satisfied if the phase shifts \( \eta_l \) fulfill

\[
cot(\eta_l(\varepsilon, \kappa)) = \frac{n_l(\kappa r)}{j_l(\kappa r)} \cdot \frac{D_l(\varepsilon) - \kappa D_n(\kappa)}{D_j(\varepsilon) - \kappa D_j(\kappa)},
\]

(3.51)

where the logarithmic derivatives are defined by

\[
D_l(\varepsilon) = \left. \frac{S}{\psi_l(\varepsilon, S)} \frac{\partial \psi_l(\varepsilon, r)}{\partial r} \right|_{r=S},
\]

(3.52)
and

$$D_n(\kappa) = \left. \frac{S}{n_l(\kappa S)} \frac{\partial n_l(\kappa r)}{\partial r} \right|_{r=S},$$

(3.53)

and correspondingly for $D_{jl}$, with $n_l$ replaced by $j_l$ in Eq. (3.53).

The tail of the muffin-tin orbital, i.e., the part in the interstitial region, obeys the expansion theorem

$$n_L(\kappa, r - R) = 4\pi \sum_{L', L''} C_{LL'} j_{L'}(\kappa, r - R') n_{L''}(\kappa, R - R'),$$

(3.54)

valid for $|r - R'| < |R - R'|$, where $n_L(\kappa, r) \equiv n_l(\kappa r) j_Y(\hat{r})$ and $j_L(\kappa, r) \equiv j_l(\kappa r) j_Y(\hat{r})$. The Gaunt coefficients $C_{LL'}$ are given by

$$C_{LL'} = \int d\hat{r} Y_L(\hat{r}) Y_{L'}(\hat{r}).$$

(3.55)

The expansion theorem (3.54) means that the tail of the muffin-tin orbital centered at site $R$ can be expanded in terms of spherical Bessel functions centered at site $R'$.

The solution of Eq. (3.45), using the muffin-tin orbitals (3.50), leads to an algebraic eigenvalue problem that is non-linear in energy and therefore cumbersome to solve. From a computational point of view it is more efficient to work with an energy-independent basis set that results in a set of linear equations.

### 3.8.2 Linearization

As the muffin-tin orbital (3.50) is constructed, its tail as well as its amplitude $\kappa n_l(\kappa S)$ and energy derivative $\kappa S n'_l(\kappa S)/n_l(\kappa S)$ at the sphere boundary depend on energy only through $\kappa$, and Eq. (3.48). Furthermore, the phase shifts (3.51) maintain continuity and differentiability for any values of $\epsilon$ and $\kappa$, and they are dependent on $\epsilon$ only because of relation (3.48) between the two. Thus, continuous and differentiable muffin-tin orbitals, Eq. (3.50), may be defined even if Eq. (3.48) is disregarded and $\kappa$ is fixed at a certain energy, i.e., $\epsilon$ and $\kappa$ are considered as separate parameters. In that way the tail as well as the muffin-tin orbital’s amplitude and derivative at the sphere boundary become energy independent. Note that $\kappa$ is a variational parameter, and frequently several muffin-tin orbitals with the same $L$ but different tail energies $\kappa$ are used in a variational procedure.

The idea of linearization, put forward by Andersen [59], is to work with a linear combination of the solution $\psi_{l,\nu}(r) \equiv \psi_l(E\nu, r)$ of the radial Schrödinger equation (3.47) evaluated at an arbitrarily chosen linearization
energy $E_{\nu}$, and its energy derivative

$$\frac{\partial}{\partial \epsilon} \psi_l(\epsilon, r) \bigg|_{\epsilon = E_{\nu}}.$$ (3.56)

$\psi_l$ and $\psi_{l,\nu}$ are orthogonal to each other as well as to the core states. They form a basis that is adapted to a particular system, suitable to calculate states within a certain energy window around the linearization energy. Note that the basis does not double in size, but the energy dependence of the basis functions is taken into account to first order in energy.

To construct a linear muffin-tin orbital, the spherical Bessel and Neumann functions $j_l$ and $n_l$ in Eq. (3.50) are replaced by the augmented functions $J_l(\kappa r)$ and $N_l(\kappa r)$,

$$\chi_{\ell}^{\text{LMT}}(\epsilon, \kappa, \mathbf{r}) = \frac{1}{\sqrt{4\pi}} \sum_{L', L} C_{L' L} j_{L'}(\kappa, \mathbf{r} - \mathbf{R}') n_{L'}^*(\kappa, \mathbf{R}' - \mathbf{R}) + \frac{\kappa}{\kappa n_L(\kappa, \mathbf{r})} J_L(\kappa, \mathbf{r}) \quad \kappa = 0.$$ (3.57)

The augmented functions $J_l$ and $N_l$ are defined by demanding that the linear muffin-tin orbital (3.57) is independent of energy around $E_{\nu}$ to first order in $(\epsilon - E_{\nu})$ in the muffin-tin sphere, i.e.,

$$\frac{\partial}{\partial \epsilon} \chi_{\ell}^{\text{LMT}}(\epsilon, \kappa, \mathbf{r}) \bigg|_{\epsilon = E_{\nu}} = 0.$$ (3.58)

This leads to the definition of the augmented spherical Bessel function

$$J_l(\kappa r) = -\frac{\psi_l(E_{\nu}, r)}{\kappa \cot(\eta_l(E_{\nu}, \kappa))},$$ (3.59)

which is continuous and differentiable everywhere and orthogonal to the core states in its own muffin-tin sphere.

By fixing $\kappa$ and disregarding relation (3.48) the tail of the muffin-tin orbital (3.50) is no longer a general solution of the Schrödinger equation (3.49) in the interstitial region. Thus, $n_l$ can be replaced by a different smooth function convenient for the problem. For the definition of the augmented spherical Neumann function $N_l$ one requires that it obeys the same expansion theorem (3.54) as $n_l$,

$$n_L(\kappa, \mathbf{r} - \mathbf{R}) = \begin{cases} 4\pi \sum_{L'} n_{L'}(\kappa, \mathbf{r} - \mathbf{R}') & |\mathbf{r} - \mathbf{R}'| \leq S \\
_k L(\kappa, \mathbf{r} - \mathbf{R}) & \forall \mathbf{R}' \neq \mathbf{R}, \text{ otherwise.} \end{cases}$$ (3.60)

The muffin-tin orbital, defined by Eqs. (3.51), (3.57), (3.59), and (3.60), is regular, continuous, and differentiable everywhere in space, and furthermore
energy independent. By expressing the tail of the muffin-tin orbital centered at \( R \) by the augmented spherical Bessel function centered at \( R' \) (Eq. (3.60)), the tail becomes orthogonal to the core states of all other muffin-tin spheres. It can now be used to formulate the solution of the Schrödinger equation (3.45) as an algebraic eigenvalue problem that is linear in energy.

### 3.8.3 The secular equation

To solve the Schrödinger equation (3.45) for a muffin-tin potential, Eq. (3.44), at a given \( k \) in reciprocal space, the wavefunction for an electronic state \( i \) with spin \( \sigma \) is expanded in terms of a set of basis functions \( \chi_{\alpha}^k \),

\[
\psi_i^\sigma(k, \mathbf{r}) = \sum_{\alpha} a_i^{k,\alpha} \chi_{\alpha}^k(E, \mathbf{r}),
\]

where the index \( \alpha \) classifying the muffin-tin orbitals has been generalized to include the spin and to allow for multiple tail energies \( \kappa \) for the same \( L \). For a crystal, the basis functions can be constructed as Bloch sums of muffin-tin orbitals,

\[
\chi_{\alpha}^k(E, \mathbf{r}) = \sum_{\mathbf{R} \neq 0} e^{i \mathbf{k} \cdot \mathbf{R}} \chi_{\alpha,}\text{LMTO}^k(E, \mathbf{r} - \mathbf{R}) + \sum_{\mathbf{R} = 0} \chi_{\alpha,}\text{LMTO}^k(E, \mathbf{r}).
\]

The solution of the Schrödinger equation can be formulated in terms of the expansion coefficients \( a_i^{k,\alpha} \), defined in Eq. (3.61), and the secular equation

\[
\sum_{\alpha'} [H_{\alpha \alpha'}^{k} - \epsilon O_{\alpha \alpha'}^{k}] a_i^{k,\alpha'} = 0,
\]

The solution of the Schrödinger equation can be formulated in terms of the expansion coefficients \( a_i^{k,\alpha} \), defined in Eq. (3.61). This leads to the secular equation

\[
\sum_{\alpha'} [H_{\alpha \alpha'}^{k} - \epsilon O_{\alpha \alpha'}^{k}] a_i^{k,\alpha'} = 0,
\]
of which there is one equation for each $\alpha$, with the Hamiltonian and overlap matrices given by
\[ H_{\alpha\alpha}^k = \langle \chi_{\alpha}^k | H | \chi_{\alpha}^k \rangle \quad \text{and} \quad O_{\alpha\alpha}^k = \langle \chi_{\alpha}^k | \chi_{\alpha}^k \rangle. \] (3.67)

Eq. (3.66) is a generalized algebraic eigenvalue problem and can be solved efficiently by standard techniques to obtain the eigenvalues $\epsilon_{\sigma k}$ and the eigenvectors $a_{\sigma k} = \{ a_{k\alpha} \}$. The wavefunction, and thus the charge density $n_{\sigma}(r)$, Eq. (3.14), can now be constructed from the expansion coefficients $a_{\sigma k}$, taking into account that only the $N = N^\uparrow + N^\downarrow$ eigenstates that are lowest in energy are occupied. The total energy for the electron system can be calculated from Eq. (3.16), expressing the kinetic energy as
\[ T_s = E_s - \sum_{\sigma} \int d^3 r V_{KS}^\sigma(r) n^\sigma(r), \] (3.68)
where $E_s$ is the sum of the $N$ lowest Kohn-Sham eigenvalues $\epsilon_{\sigma k}$. The numerical problems related to the calculation of the eigenvalue sum will be discussed in Section 4.5.

### 3.9 Full-potential LMTO

The greater part of the calculations presented in this work were done with the fully-relativistic implementation of the full-potential LMTO (FP-LMTO) method by John Wills [60]. In the FP-LMTO method the shape of the potential is not restricted to be of the muffin-tin type, Eq. (3.44). Although the actual implementation of such a method is a cumbersome task, the basic ideas are very simple. In the previous section it was shown that the solution of the Kohn-Sham equations can be formulated as an eigenvalue problem expressed through matrix elements of the Hamiltonian, and hence the potential, in a fixed basis. In a full-potential method one simply calculates the matrix elements using the full potential, which is expanded in spherical harmonics inside the spheres and in a Fourier series in the interstitial region. For example, inside each muffin-tin sphere the potential is written as
\[ V(r) = \sum_{L} V_l(r) Y_L(\hat{r}). \] (3.69)

The matrix elements $H_{\alpha\alpha}^k$, Eq. (3.67), can then be calculated as integrals over the $V_l(r)$. 35
3.10 Relativistic effects

The presentation in this chapter is based on the non-relativistic Schrödinger equation, Eqs. (3.1) and (3.5). Relativistic effects, which have been neglected throughout the discussion so far, are essential for heavy atoms. Furthermore, the spin-orbit coupling, an interaction between the electron’s spin and spatial degrees of freedom, is the microscopic origin of the magnetic anisotropy discussed in Section 4.3.

The adequate description of electrons is through the Dirac equation that involves a four-component wavefunction describing spin-\(\frac{1}{2}\) particles. The numerical solution of the Dirac equation is, however, more cumbersome. In the limit of low velocities the Dirac equation reduces to the Schrödinger equation, Eqs. (3.1) and (3.5), plus relativistic corrections. The two scalar-relativistic corrections, which are independent of the spin \(s\), are the mass-velocity and the Darwin term. The first is a correction due to the relativistic variation of mass with velocity, and the latter comes from the fact that the electron is not a point particle, but spread out over a volume of the order of \(\left(\frac{\hbar}{m_e c}\right)^3\). The Darwin term is non-zero only for the \(s\) electrons. The third relativistic correction is the spin-orbit coupling,

\[
\hat{H}_{so} = -\frac{2}{c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{I} \cdot \mathbf{s},
\]

which is the interaction of the spin magnetic moment with the magnetic field created by its motion around the nucleus. Because of its dependence on \(1/r\) and on the gradient of the potential, \(dV/dr\), it is most important close to the nucleus, i.e., for the core electrons.
4. Materials for magnetic data storage and magnetic anisotropy

In this chapter properties of magnetic materials are discussed, with a focus on materials that are of interest in magnetic data storage applications. After an introduction to magnetism and magnetic materials, which follows the overview given by Bruno [61], a short background on magnetic data storage will be given in Section 4.2. Then, in Section 4.3, the physics behind magnetic anisotropy is discussed, including a phenomenological description in terms of magnetic anisotropy constants. Section 4.4 covers the magneto-elastic coupling. The calculation of magnetic anisotropy energies from first principles is the subject of Section 4.5, and the results from Papers III to IX are summarized in Section 4.6.

4.1 Introduction

One of the two characteristic properties of ferromagnetic materials is the imbalance in occupation of the spin-up and spin-down electronic states, which is manifested in the existence of a magnetic moment and, disregarding the occurrence of magnetic domains, a spontaneous magnetization. The energy involved in the splitting of the spin-up and the spin-down states of a magnetic material with a Curie temperature of 1200 K is of the order of \( k_B T_C \approx 0.1 \text{ eV/atom} \). The second characteristic property is the so-called magnetic anisotropy that makes the energy of a magnetic material dependent on the direction of its magnetization with respect to its crystal lattice. The energies involved in this symmetry breaking are of the order of \( 10^{-6} \text{–} 10^{-3} \text{ eV/atom} \), and are hence of an order that makes magnetic anisotropy noticeable in everyday life. It is the magnetic anisotropy that contributes to the persistence of a spontaneous magnetization in permanent magnets, thereby keeping a magnet stick to the refrigerator door. Also, magnetic anisotropy is essential in magnetic data storage, i.e., computer hard disk drives, where it prevents the loss of information stored as bits in small grains of a magnetic material. In contrast to these magnetically hard materials, soft materials with a small, preferably vanishing magnetic anisotropy energy (MAE), are sought after for use in transformer cores, to minimize hysteresis losses, and in magnetic sensors.
that are, e. g., used to read out the information stored in a hard disk drive. An important property sought after in both soft and hard magnetic materials is of course a sufficiently high ordering temperature, so that the magnetic properties persist at room temperature. Practically, this means that most materials that are of interest are ferromagnets with a large saturation magnetization and a Curie temperature well above room temperature.

4.2 Magnetic data storage

The storage of information and its fast accessibility has become indispensable in everyday life. The greater part of information is recorded magnetically in computer hard disk drives, where each bit of information, i. e., a logical zero or one, is stored as a direction of magnetization in a small volume of a granular recording medium. In order to improve the signal-to-noise ratio in the readout process, this volume typically consist of a few hundred magnetic grains. In each of these weakly coupled ferromagnetic grains, with a diameter of about 10 nm, the magnetization can point in either of two directions, confined to be in the film plane (longitudinal recording) or perpendicular to it. The requirements on the recording medium, which is the surface layer of a spinning disc, are that the information can be written into the medium by a write head, is preserved for a macroscopic time scale at a temperature 50–100 K above room temperature, and can be read from the medium by a read head. All three main ingredients of a hard disk drive, the recording medium as well as the write and read heads, are based on magnetic materials. The rapid increase in areal density, i. e., the amount of information that can be stored per unit area, is—at least in part—due to advances in the engineering of these materials.

The first commercial hard disk drive was released by IBM in 1956. The RAMAC consist of fifty 24-inch disks that could hold five Mbytes of information, just enough to store one picture of a modern digital camera or two to three songs in a compressed audio format. Since then the recording density of hard disk drives has increased by almost eight orders of magnitude, and areal densities exceeding 100 Gbits/in² have been demonstrated. Modern hard disk drives have the ability to store several hundreds of Gbytes. This remarkable increase in the areal density has mainly been achieved by a simple scaling of all dimensions [62]—scaling all linear dimensions by a factor of $s$ yields an $s^{-2}$ increase in the areal density. This traditional scaling, however, is limited by the onset of superparamagnetism in the recording layer [62, 63], as the magnetic energy per grain, $K_u V$, where $V$ is the grain volume and $K_u$ the uniaxial MAE, is decreased by $s^{-3}$. At non-zero temperature, the direction of magnetization fluctuates randomly around its equilibrium with an average energy of $k_B T$ at a frequency of a few tens of gigahertz. The rate of random
reversals can be estimated from this resonant frequency times a Boltzmann factor, \( \exp\left(\frac{K_u V}{k_B T}\right) \). Because of the exponential dependence on the grain volume, already a scaling with \( s = 2 \) can reduce the average time between random reversals dramatically, and the recorded information is erased by thermal fluctuations in an intolerable short time if \( K_u V/k_B T \) becomes too small. An estimate for the stability of the stored information against thermal agitation requires \( K_u V/k_B T \approx 50–70 \) and sets the superparamagnetic limit for conventional magnetic recording media at 40–100 Gbits/in\(^2\) [63, 64, 65].

An avenue to further decrease the grain volume in future ultrahigh-density recording media, while maintaining the integrity of the recorded data, is the usage of high-\( K_u \) materials [65], with an MAE that is one to two orders of magnitude higher than that of today's recording media, which are based on hexagonal Co alloys. However, the maximum practical MAE is limited by the required write-field

\[
H_w \approx \frac{K_u}{M_s},
\]

where \( M_s \) is the medium’s saturation magnetization, that must be delivered by the writer. This, in turn, is limited by the writer’s saturation magnetization and its geometry. In addition, the amplitude of the magnetic field emanating from recorded data scales with the product of \( M_s \) and the thickness of the recording layer. Hence, a larger \( M_s \) increases the field available at the readback process. Thus, a large saturation magnetization is an essential feature of new materials for both future recording media as well as write heads. Despite a great effort to find new materials with a larger saturation magnetization, the record in saturation field is still held by an \( Fe_{0.7}Co_{0.3} \) alloy, the maximum of the Slater-Pauling curve [6].

Today's hard disk drives are based on antiferromagnetically-coupled recording (AFC) media [66], that push the superparamagnetic limit to higher areal densities. In an AFC medium the effective volume of the grains, and hence the magnetic energy, is increased by coupling two ferromagnetic layers through a thin Rh layer such that the individual grains are coupled antiferromagnetically. The antiparallel orientation of the individual layers reduces the demagnetizing fields and makes the multilayer structure appear magnetically thinner than it is, while the magnetic energy per grain is increased. A similar approach to increase the magnetic energy per grain is by thermally assisted recording [67] into exchange-spring [68] materials. In FeRh/FePt thin films [69], e.g., the large MAE is provided by the FePt layer, whereas the large moment that is necessary to flip the magnetization direction is provided by the FeRh layer that is exchange-coupled to the FePt layer. The latter is antiferromagnetic at room temperature but becomes ferromagnetic with a large saturation moment and a small MAE upon heating above a transition temperature, thereby lowering the required write field, Eq. (4.1).
The steepened increase in the areal density versus time that happened in the 90’s was mainly due to the introduction of magnetoresistive and, less than a decade after the discovery of the GMR effect [70, 71], giant-magnetoresistive read heads. This latter development is an example of the success of devices that are based on advanced magnetic materials in industrial applications. Apart from a high signal-to-noise ratio, i.e., a large GMR effect, these sensors are required to respond easily to the changing magnetic field due the bit pattern of the disk spinning underneath it. Read heads usually consist of a pinned magnetic layer and, separated by a non-magnetic layer, a layer that can move freely. The free layer is an example for the use of soft magnetic materials. A new generation of read heads is based on tunneling magneto-resistive (TMR) sensors, in which the non-magnetic layer is insulating, resulting in a larger magnetoresistance.

4.3 The physics of magnetic anisotropy

The microscopic origin of the magnetic anisotropy is twofold. One is the relativistic spin-orbit coupling, Eq. (3.70), that couples the electron’s spin to its spatial degrees of freedom, which, in turn, are linked to the crystal lattice. The other is the dipole-dipole interaction between the magnetic moments that the spin and orbital moments give rise to. In a real magnetic sample there are two distinct contributions to the MAE, the intrinsic magneto-crystalline anisotropy, and a contribution that depends on the shape of the specimen, known as the shape anisotropy. The latter originates solely from the dipole-dipole contribution to the MAE, whereas the magneto-crystalline anisotropy originates from both contributions. In a plate-shaped magnetic sample, e.g., a thin film, the shape anisotropy always favors an orientation of the magnetization parallel to the plate. In the following the discussion will be limited to the magneto-crystalline anisotropy, and it is this contribution only that is referred to as the MAE.

For a phenomenological description of the MAE it is convenient to expand the Gibbs free energy $G(T, H_M, \mathbf{M}, \varepsilon)$, where $H_M$ is the projection of the external field on the magnetization direction $\mathbf{M}$ and $\varepsilon$ is the strain tensor, in successive powers of the components $(\alpha_1, \alpha_2, \alpha_3)$ of $\mathbf{M}$. Note that the expansion contains only even powers of $\alpha$ because of the time-reversal symmetry. In addition to that, the crystal symmetry imposes some relationships and reduces the number of independent parameters. For a cubic symmetry the Gibbs free energy is usually written as

$$
G_{\text{cryst}} = K_0 + K_1 (\alpha_1^2 \alpha_2^2 + \alpha_3^2 \alpha_1^2 + \alpha_2^2 \alpha_3^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2 + K_3 (\alpha_1^2 \alpha_2^2 + \alpha_3^2 \alpha_1^2 + \alpha_2^2 \alpha_3^2)^2 \ldots,
$$

(4.2)
where the $\alpha_i$ are the magnetization’s components along the cubic axes and the $K_i$ are the anisotropy constants. Note that in a cubic system, such as bcc Fe and fcc Ni, the lowest order anisotropy constant is of fourth order. In a tetragonal system on the other hand, with $a = b \neq c$, such as the tetragonal structures considered in Paper III, the Fe-Co alloys considered in Papers IV and V, and the chemically ordered L10 FePt alloy in Paper VI, the second order term is not forbidden and the lowest order term is $K_0 \alpha_i^2$, where $K_0$ is the uniaxial anisotropy constant. For systems with a hexagonal symmetry, such as hcp Co and hcp Gd, the Gibbs free energy can be expanded as

$$G_{\text{cryst}} = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta + (K_3 + K'_3 \cos(6\phi)) \sin^6 \theta \ldots , \quad (4.3)$$

where $\theta$ and $\phi$ specify the direction of the magnetization with respect to the $c$ and $a$ axes, respectively. Usually only a few anisotropy constants are sufficient to describe the MAE of a system, as Eq. (4.2) and (4.3) are rapidly converging series. The fast decrease of the anisotropy constants with increasing order will be illustrated with a perturbation theory argument later on. Frequently, only the lowest order constant is discussed together with the so-called easy axis, which is the direction of magnetization that gives the lowest energy, in contrast to the hard axis. As an example, $K_1$ is of the order of 1 $\mu$eV/atom in bcc Fe and fcc Ni, where the easy axis is along [100] in Fe and along [111] in Ni. In hcp Co, $K_1$ is a second-order constant of about 60 $\mu$eV/atom with the easy axis oriented along [0001], i.e., the $c$ axis.

Already Néel [72] pointed out that the local symmetry of atoms located at a surface or interface is lower than that of the atoms in the bulk. Hence, anisotropy constants of lower order might be present at the interface and contribute to the total magnetic anisotropy. This becomes particularly important in thin films and multilayers in which a considerable amount of the atoms are located at an interface or at the surface. The total magnetic anisotropy is then a sum of a volume contribution and an interface contribution.

In order to evaluate the contribution of the spin-orbit coupling to the magnetic anisotropy, it is instructive to treat it by perturbation theory. For a uniaxial system, the change in energy to second order in the spin-orbit coupling $\hat{H}_{\text{so}}$, defined in Eq. (3.70), is given by

$$\Delta E = \sum_{o,u} \frac{|\langle u | \hat{H}_{\text{so}} | o \rangle|^2}{E_o - E_u} , \quad (4.4)$$

where $o$ and $u$ denote the occupied and unoccupied electronic states, respectively. Extending the expression to higher orders in $\hat{H}_{\text{so}}$, a general estimate for an anisotropy constant of order $n$ is obtained:

$$K \approx \xi_n \frac{\xi}{W^{n-1}} = \xi \left( \frac{\xi}{W} \right)^{n-1} , \quad (4.5)$$

where the $\alpha_i$ are the magnetization’s components along the cubic axes and the $K_i$ are the anisotropy constants. Note that in a cubic system, such as bcc Fe and fcc Ni, the lowest order anisotropy constant is of fourth order. In a tetragonal system on the other hand, with $a = b \neq c$, such as the tetragonal structures considered in Paper III, the Fe-Co alloys considered in Papers IV and V, and the chemically ordered L10 FePt alloy in Paper VI, the second order term is not forbidden and the lowest order term is $K_0 \alpha_i^2$, where $K_0$ is the uniaxial anisotropy constant. For systems with a hexagonal symmetry, such as hcp Co and hcp Gd, the Gibbs free energy can be expanded as

$$G_{\text{cryst}} = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta + (K_3 + K'_3 \cos(6\phi)) \sin^6 \theta \ldots , \quad (4.3)$$

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where $o$ and $u$ denote the occupied and unoccupied electronic states, respectively. Extending the expression to higher orders in $\hat{H}_{\text{so}}$, a general estimate for an anisotropy constant of order $n$ is obtained:
where $W$ is the bandwidth and $\xi$ is the spin-orbit coupling strength (cf. Eq. (3.70)),

$$\hat{H}_{so} = \xi \mathbf{l} \cdot \mathbf{s}. \quad (4.6)$$

For the magnetic transition metals, the magnetic moment, and hence the MAE, is dominated by the 3$d$ electrons, and $\xi_{3d}$ is of the order of 50–100 meV. The 3$d$ bandwidth $W$ is of the order of 5 eV. Thus, a rough estimate for the MAE in a uniaxial system ($n = 2$) is 1 meV/atom, and for a cubic system ($n = 4$) 0.3 $\mu$eV/atom, which is in good agreement with the values given above. Also, the fast convergence of the expansions (4.2) and (4.3), i.e., the fast decrease of the anisotropy constants with increasing order, can be understood from Eq. (4.5), since $\xi/W \ll 1$.

The dipolar crystalline anisotropy contributes only to anisotropy constants of second order and vanishes therefore in cubic systems, but they might become important for structures of lower symmetry. In the tetragonal transition metals studied in Paper III its contribution to the total magnetic anisotropy is negligible. For systems with an hcp structure the dipolar crystalline anisotropy vanishes close to the ideal ratio $c/a = \sqrt{8/3} \approx 1.633$. In hcp Co, with $c/a = 1.622$, the dipolar contribution is of the order of 0.4 $\mu$eV/atom and is much smaller than that from the spin-orbit coupling. It is, however, substantial in hcp Gd, which has $c/a = 1.6$ and a large magnetic moment of more than 7 $\mu_B$, as it scales quadratically with the magnetic moment [Paper IX].

### 4.4 Magneto-elastic coupling

In the expansion of Gibbs free energy in Eqs. (4.2) and (4.3), only changes with respect to the direction of the magnetization relative to the crystal lattice were considered. It is, however, a function of the strain tensor $\varepsilon$ as well, which so far was assumed to be zero. In a magnetized and strained system new energy terms occur that depend both on the direction of magnetization and the strain, the magneto-elastic energy. The term of lowest order in the expansion of the magneto-elastic energy that is non-vanishing is linear with respect to $\varepsilon$ and quadratic with respect to the $\alpha_i$'s. As for the expansions discussed above, the number of independent magneto-elastic coefficients are reduced by symmetry constraints. For a cubic system the expansion is written as

$$G_{\text{mag–el}} = B_1 (\varepsilon_{11} \alpha_1^2 + \varepsilon_{22} \alpha_2^2 + \varepsilon_{33} \alpha_3^2) + 2B_2 (\varepsilon_{12} \alpha_1 \alpha_2 + \varepsilon_{23} \alpha_2 \alpha_3 + \varepsilon_{31} \alpha_3 \alpha_1) + \ldots \quad (4.7)$$

As the symmetry is generally lowered under strain, anisotropy contributions of lower order that are forbidden in the unstrained stated might become im-
portant. Since the anisotropy constants become larger with decreasing order, even small strains can give rise to large magnetic anisotropies. In Paper III the magnetic anisotropy of the strained ferromagnetic transition metals Fe, Co, and Ni was studied.

While a system under strain acquires magnetic anisotropy, the converse is also true: the mere existence of a magnetization along a given direction induces an anisotropic strain, the so-called magnetostriction. This can be understood from the fact that the magneto-elastic energy is linear with respect to $\varepsilon$. Thus, a system can always minimize its energy by a non-vanishing strain. This is of course balanced by the elastic energy which is quadratic with respect to $\varepsilon$, and can be expanded for a cubic system as

$$G_{el} = \frac{1}{2} C_{11} (\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + C_{12} (\varepsilon_{11} \varepsilon_{22} + \varepsilon_{22} \varepsilon_{33} + \varepsilon_{33} \varepsilon_{11})$$

$$+ \frac{1}{2} C_{44} (\varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{31}^2).$$  \hspace{1cm} (4.8)

Minimizing the sum of the elastic and magneto-elastic contributions, $G_{el} + G_{mag–el}$, gives the spontaneous magnetostriction for a cubic system:

$$\frac{\delta l}{l} = \frac{3}{2} \lambda_{100} \left( \alpha_1^2 \beta_1^2 + \alpha_2^2 \beta_2^2 + \alpha_3^2 \beta_3^2 - \frac{1}{3} \right)$$

$$+ 3 \lambda_{111} (\alpha_1 \alpha_2 \beta_1 \beta_2 + \alpha_2 \alpha_3 \beta_2 \beta_3 + \alpha_3 \alpha_1 \beta_3 \beta_1),$$  \hspace{1cm} (4.9)

where $\lambda_{100}$ and $\lambda_{111}$ are the magnetostriction constants,

$$\lambda_{100} = -\frac{2B_1}{3(C_{11} - C_{12})},$$

$$\lambda_{111} = -\frac{B_2}{3C_{44}}.$$  \hspace{1cm} (4.10)

The meaning of Eqs. (4.9) and (4.10) is as follows: if a cubic structure is brought from a demagnetized state to a state with the magnetization along the direction ($\alpha_1, \alpha_2, \alpha_3$), its length along the direction ($\beta_1, \beta_2, \beta_3$) changes by $\delta l/l$. The change of length for a body magnetized along [100] ([111]) is then simply equal to $\lambda_{100}$ ($\lambda_{111}$). In the cubic ferromagnetic transition metals, $\lambda_{100}$ and $\lambda_{111}$ are of the order of $10^{-5}$, but reach considerably larger values of the order of $10^{-3}$ in some rare-earth-Fe$_2$ Laves phases [73].

4.5 Magnetic anisotropy from first principles

In the previous section it was stated that the magnetic anisotropy energy $\Delta E$ is defined as the difference in energy of a system with the magnetization aligned along two inequivalent directions. Thus, it can be evaluated as the total energy

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where \( E^{a(b)} \) is the total energy with the magnetization aligned along \( a(b) \).

What sounds like a trivial task is complicated by the small energy differences typical for magnetic anisotropies, ranging from a few \( \mu \text{eV} \) in the case of the cubic transition metals [74] to a few meV in transition metal compounds like FePt [Paper VI] and SmCo5 [75]. The total energies of the transition metals are of the order of several \( 10^4 \) eV/atom, i.e., about seven to ten orders of magnitude larger than the energy difference associated with the magnetic anisotropy. Hence, the calculation of magnetic anisotropy energies is a difficult task that puts stringent requirements on the numerical accuracy of a density functional calculation. Often the electronic states close to the Fermi surface make the most important contribution to the magnetic anisotropy [76].

In order to describe these states in a satisfactory way the Brillouin zone has to be sampled with great care, i.e., the Kohn-Sham equation has to be evaluated for a large number of \( k \) points in reciprocal space (cf. Section 3.7). Luckily, a shortcut exists that can be used to reduce the computationally effort considerably. The force theorem states that the total energy difference, Eq. (4.11), can be approximated by the difference of the eigenvalue sums \( E_s \), introduced in the discussion around Eq. (3.68), for the two magnetization directions [77],

\[
\Delta E \approx E^a_s - E^b_s. \tag{4.12}
\]

In practice, the self-consistent potential is calculated with a scalar-relativistic Hamiltonian, i.e., without the spin-orbit coupling. Then, in a subsequent step, the eigenvalues are calculated using the fully-relativistic Hamiltonian with the magnetization aligned along \( a \) and \( b \), respectively. The computational advantage lies in the fact that the secular equation (3.66) has to be solved for a large number of \( k \) points only once for each magnetization direction, and that the number of \( k \) points necessary for the calculation of the self-consistent potential is one to two orders of magnitude smaller.

As stated above, the small energy differences involved in the calculation of magnetic anisotropy energies require careful tests of the results with respect to numerical parameters. It turns out that the most important aspect is the Brillouin zone integration, i.e., the calculation of the eigenvalue sums in Eq. (4.12). Apart from the number of \( k \) points, the treatment of the eigenvalues in the vicinity of the Fermi surface is crucial for the calculation of magnetic anisotropy energies. To minimize the numerical inaccuracy related to the discrete sampling of the Brillouin zone, the eigenvalue sums are calculated as (omitting the index for the magnetization direction)

\[
E_s = \sum_{\sigma, k, i} w^{\sigma, k}_{i} \varepsilon^{\sigma, k}_{i}, \tag{4.13}
\]
Figure 4.1: Convergence of the magnetic anisotropy energy of fct Co, $c/a = 1.1$, with respect to the number of $k$ points for different Brillouin zone integration techniques. The smearing widths used for the GBM are indicated in the plot (in mRy)

where the $w_{\sigma,k}^{\alpha}$ are weight factors that can be calculated in different ways. In the linear tetrahedron method [78] the reciprocal space is divided into corner sharing tetrahedra, the corners being the $k$ points. For those $k$ points that belong to tetrahedra that are not dissected by the Fermi surface the weight factors are set to unity or zero, if the tetrahedron is located below or above the Fermi surface, respectively. For all tetrahedra that are dissected by the Fermi surface, the weight factors are calculated according to a linear interpolation within the tetrahedron, i.e., the portion of the Fermi surface within the tetrahedron is approximated by a plane such that the occupied volume is preserved. In the modified tetrahedron method due to Blöchl the interpolation goes beyond the linear approximation [56]. Another route to treat the eigenvalues close to the Fermi surface are smearing methods, in which the weight factors are calculated from some kind of smooth function centered at the Fermi surface that replaces the step function. The most popular choices for these smearing functions are the Fermi-Dirac and the Gaussian distribution functions.

The calculated magnetic anisotropy energies are sensitively dependent on the method used to calculate the eigenvalue sums. As an example, the convergence of the magnetic anisotropy of face-centered tetragonal (fct) Co is shown in Fig. 4.1 for different Brillouin zone integration methods, the modified tetrahedron method [56] (MTM) and the Gaussian broadening method [79] (GBM). From Fig. 4.1, and further examples that can be found in Papers III and VI, it becomes apparent that the width of the smearing function is an important convergence parameter and has to be checked
carefully. A particularly instructive example is the convergence of the magnetic anisotropy energy of hcp Co, shown in Fig. 4.2. In this case even the sign is dependent on the Brillouin zone integration, which might explain the inconsistent values found in literature [80]. In the case of hcp Gd [Paper IX], it was found that the calculated MAE is sensitively dependent even on the Brillouin zone integration performed during the calculation of the self-consistent potential that is used as a starting point for the force theorem calculations. A general conclusion is that the Gaussian broadening method gives comparable results to the tetrahedron method if a small smearing is used, thereby loosing the advantage of the faster convergence with respect to the number of \( k \) points. A problem inherent to the GBM, besides the fact that details of the Fermi surface that are important for the magnetic anisotropy might be smeared out, is the incorrect position of the Fermi energy. Methfessel and Paxton advised a way to overcome the latter problem by using higher order terms in the expansion of the delta function in Hermite polynomials, in which the simple Gaussian is the lowest order [79].

Another important question is which kind of exchange correlation potential should be used for magnetic anisotropy calculations. While some studies concerning the choice of exchange correlation potentials exist, no general conclusion can be drawn. As an example, the uniaxial magnetic anisotropy energy of tetragonal Fe, Co, and Ni (cf. Paper III) is shown in Fig. 4.3 for both LDA and GGA. Comparing the calculated values with the experimentally determined values one can draw the conclusion that the magnetic anisotropy of Fe, Co,
Figure 4.3: Uniaxial magnetic anisotropy energy of tetragonal Fe, Co, and Ni, calculated with two different exchange correlation potentials, LDA and GGA, at their respective experimental volume (cf. Paper III). The squares indicate experimental results [81, 82, 83].
and Ni, at their respective experimental volume, is better described by the LDA.

4.6 Summary of Papers III to IX

4.6.1 Tetragonal and trigonal Fe, Co, and Ni

In Paper III the uniaxial MAE of tetragonal and trigonal structures of the ferromagnetic transition metals Fe, Co, and Ni was studied. As is expected from the discussion around the expansion of the MAE in terms of anisotropy constants and the estimates obtained from perturbation theory in Section 4.3, the MAE is found to increase strongly when the cubic symmetry is broken. For tetragonal structures of Co and Ni a regular behavior of the MAE is observed, i.e., only the symmetry dictated nodes at the cubic structures appear along this path of distortion that connects the bcc and the fcc structure. In the case of Fe, however, two additional changes of the easy axis of magnetization occur. This anomaly is analyzed in terms of the eigenvalues of tetragonal Fe at the high-symmetry $\Gamma$ point—the center of the Brillouin zone—and can be attributed to a topological change of the Fermi surface upon distortion.

4.6.2 Tetragonal Fe-Co alloys

From the analysis of the eigenvalues of tetragonal Fe at the $\Gamma$ point presented in Paper III one can draw the conclusion, using an argument based on perturbation theory similar to that outlined in Section 4.3, that an enhanced uniaxial MAE can be expected in tetragonal Fe-Co alloys [Paper IV]. This is the case if the $c/a$ ratio and the alloy concentration are chosen such that two specific eigenvalues—one that is occupied at structures close to bcc Fe and becomes unoccupied if the unit cell is distorted towards fcc, and one for which the opposite holds true—cross at the Fermi level. Since the MAE, according to Eq. (4.4), is inversely proportional to the energy difference of the occupied and the unoccupied states, a strongly increased MAE is expected if this condition is met. From a simple rigid band approach the maximum MAE should occur for $c/a \approx 1.22$, where $c/a = 1$ corresponds to bcc and $c/a = \sqrt{2} \approx 1.41$ corresponds to fcc, respectively, and for an alloy concentration of 50% Fe and 50% Co. The full calculations presented in Paper IV yield a maximum in the MAE of 0.8 meV/atom at $c/a = 1.20$–1.25 and a concentration of 60% Fe, in fair agreement with the rigid-band estimate. In these calculations the Fe-Co alloy is modeled by the virtual crystal approximation (VCA), which is expected to hold for the present case. In comparison with other materials that have been considered for magnetic recording applications [65], the suggested alloy has as 50% larger MAE and a 50% larger saturation magnetization than
Figure 4.4: Saturation magnetic moment (upper) and magnetic anisotropy energy (lower) of an (Fe,Co)$_3$/Pt$_5$ superlattice (filled circles). The open circles are the results from a calculation for an Fe-Co alloy using the structural data of the Fe-Co layers in the superlattice. The dashed line in the upper plot shows the total magnetic moment, i.e., including the induced moments in the Pt layers. The experimental data from Paper V is shown by squares.

L1$_0$ FePt, a compound that has received considerable attention recently, and which is studied in Paper VI. Note that the easy axis of magnetization is along the $c$ axis, which facilitates the use in perpendicular recording applications, and that the MAE can easily be tailored by adjusting the alloy composition. From a technological point of view, a great advantage of the suggested alloy is the lower growth temperature as compared to FePt. In the latter the MAE is due to the layered structural arrangement of the Fe and Pt atoms, for which a deposition temperature of 500–600$^\circ$C is required, whereas the MAE in the Fe-Co alloys does not require an ordered state.

That the suggested tetragonal Fe-Co alloys can be accomplished, albeit with a non-optimal $c/a$ ratio, was demonstrated in Paper V, and a strongly enhanced MAE was indeed found. In order to achieve the tetragonal structure that is crucial for the large MAE, an Fe-Co alloy with 64% Co was grown in conjunction with Pt in a superlattice, comprising three monolayers (Fe,Co) and five monolayers of Pt. The role of Pt in the superlattice is to force the
Fe-Co layers to adapt a tetragonal structure. The measured MAE amounts to 0.2 meV/Fe-Co-atom, which is about half of the value that was obtained from first-principles calculations similar to those of Paper IV, using the structure of the real sample. The agreement between the experimentally determined MAE and the calculated value is satisfactory, considering the fact that the calculations were done for a perfect sample, neglecting interface roughness and alike.

In addition to the results presented in Paper V the saturation magnetization and the MAE for the (Fe,Co)$_3$/Pt$_5$ superlattice were calculated for the whole concentration range. From the results shown in Fig. 4.4 one can see that the maximum MAE for the superlattice is not expected at the concentration of the actual sample, but at a Co concentration around 40%. Considering this, and the fact that the $c/a$ in this sample is not at optimum, an even higher MAE might be achieved by other means. Also shown in Fig. 4.4 are the saturation magnetization and the MAE of an Fe-Co alloy of the same structure, i.e., volume and $c/a$, as the Fe-Co layers in the superlattice. By comparison one can separate the structural influence of the Pt layers in the superlattice, i.e., inducing the desired structure of the Fe-Co layers, from the electronic effect that the adjacent Pt layers have on the MAE. It may be seen from Fig. 4.4 that the latter effect is less important for the general trend of the MAE, with the most pronounced effect being an increase of the total magnetic moment and a shift of the conspicuous maximum in the MAE to lower Co concentrations.

4.6.3 L1$_0$ FePt and (Fe,Mn)Pt

In Paper VI chemically ordered FePt was studied. FePt crystallizes in the L1$_0$ structure, which is a face-centered tetragonal unit cell with the corners and faces occupied by the two distinct types of atoms. FePt has received a lot of attention recently, because of its large uniaxial MAE of 2.8 meV/f.u., and has been discussed as a potential candidate for ultrahigh-density magnetic recording media [65]. FePt has also been studied as a building block of exchange-spring magnets [69, 84].

The focus in Paper VI is on the microscopic origin of the large MAE and its dependence on long-range chemical order. It was found that, although the large MAE mainly originates from the Fe atoms, it is the strong spin-orbit coupling on the Pt atoms that is responsible for the large MAE. The effect of compositional disorder on the MAE was studied within the coherent potential approximation (CPA), and it was found that a non-complete chemical order strongly reduces the MAE. Furthermore, the MAE of (Fe,Mn)Pt, with a random Fe-Mn alloy on the Fe sublattice, was studied within the VCA, the CPA, and by supercell calculations. The MAE increases within the concentration range studied and reaches a value that is 33% larger than that of pure FePt for
4.6.4 Fe/Co(001) superlattices

In Paper VII we studied the magnetic properties of Fe/Co(001) superlattices. An increase of the total magnetic moment with Co concentration was found for Fe-rich superlattices, similar to what is observed in bulk bcc Fe-Co alloys [6]. The maximum in magnetic moment is, however, shifted towards lower Co concentrations. The increase in total moment is due to an enhanced magnetic moment of the Fe atoms that are close to the Fe-Co interface. The tetragonal structural distortion and the roughness of the interface have only a minor effect on the magnetic moments. Furthermore, the magnetic anisotropy was calculated, and the easy axis of magnetization was found to be within the film plane for all compositions studied, with a transition from the [100] direction for Fe-rich superlattices to the [110] direction at about 50% Co.

4.6.5 Rare-earth/Cr/Fe multilayers

Despite their large saturation magnetic moments, the rare-earth metals are of limited use for technical applications. This is mainly due to their low ordering temperatures, Gd having the highest of just above room temperature among them. The ferromagnetic transition metals on the other hand, and especially Fe and Co, have Curie temperatures of the order of 1000 K. In Paper VIII the question is raised whether these two important properties of magnetic materials, i.e., a large Curie temperature and a large saturation magnetization, can be combined in a single material. The materials considered in this study are multilayers comprising a rare-earth monolayer on bulk Fe, separated by a monolayer of Cr. The reason for choosing this particular structure is the observed antiparallel coupling of the magnetic moments at the interfaces between Fe and Cr, and between the rare-earths and the transition metals, respectively, which should result in an effective ferromagnetic coupling between the rare-earth and the Fe layers. From the study presented in Paper VIII, for which the rare-earth metals Gd, Dy, and Tb were considered, it was concluded that such a ferromagnetic coupling can indeed be obtained, with an ordering temperature that is of the same order as that of the ferromagnetic transition metals.

4.6.6 hcp Gd

The MAE of hcp Gd has been a long-standing problem and is addressed in Paper IX. Gd is different from the other rare-earth metals in that the charge distribution of the localized $4f$ shell, which is in an $S$ state, is spherical. Thus, the interaction between the multipole moments of the $4f$ charge cloud with the crystalline electric field, which is the principal source of the MAE in the
other rare-earths metals, is absent in Gd. Instead, the two main contributions to the MAE are the dipole-dipole interaction of the $4f$ moments and the spin-orbit interaction of the itinerant electrons. The appearance of higher-order contributions to the MAE is due to the polarization of the conduction band via the exchange interaction with the $4f$ electrons. The peculiar temperature dependence of the easy axis of magnetization was successfully modeled in a qualitative way by calculating the MAE as a function of a reduced $4f$ moment, designed to simulate the reduction of the magnetic moment with temperature. Furthermore, it was found that the appearance of an easy axis of magnetization at an angle off the $c$ axis at low temperature depends sensitively on the way the Brillouin zone integration is performed.
5. Conclusions and outlook

Advanced materials, such as new alloys and compounds, and materials that are chemically modulated or limited in size in one or more dimensions, become increasingly important. It is not only the scientific community that has discovered these additional degrees of freedom in the tailoring of materials in order to study fundamental problems of physics, but these new materials also gain importance in everyday life. Both the storage and the transfer of information relies, to a certain extend, on devices build of hetero-structures, such as GMR sensors and quantum well lasers.

Parallel to the improvement of growth techniques, computational methods based on the density functional theory are continuously developed and improved. They contribute both to the understanding of material’s properties on a microscopic level, and allow to perform studies of realistic materials. The latter has become possible due to the steadily increasing computational power that is available to the scientific community, since the increasing complexity of new materials is also reflected in the complexity of first-principles calculations.

The tetragonal Fe-Co alloys that are studied in Papers IV and V are a good example for the fruitful interplay between computational and experimental physics. Based on first-principles calculations these alloys were predicted as a new material with a large uniaxial magnetic anisotropy energy, something which was confirmed subsequently by experimental studies. Also, the mechanism responsible for the unusually large magnetic anisotropy energy was identified with the help of first-principles calculations. To achieve a true understanding of the observed properties is the ultimate goal, and is of course much more satisfactory than a mere search for new materials.

Just recently, magnetic superlattices deposited on nano-spheres were suggested as a new type of material [85]. The deposition of magnetic superlattices on a curved substrate offers a new degree of freedom in materials design, since it allows to achieve a local variation of strain and interlayer distance throughout the sample, and hence to tailor new materials. For first-principles studies of these type of material, and advanced materials in general, it will be essential to move from idealized structures and interfaces to realistic ones.
Material för magnetisk informationslagring

Denna avhandling består av två delar, en som är baserad på experimentella rön och en del som kretsar kring så kallade första-princip-beräkningar av magnetiska material.


Den andra delen av denna avhandling handlar om första-princip-beräkningar av egenskaper hos magnetiska material. Utgångspunkten för en sådan beräkning är enbart vilka typer av grundämnen, d. v. s. deras kärnladdningstal, som ingår i materialet som ska studeras. I praktiken
används ofta även den experimentellt vedertagna kristallstrukturen. Sedan
används en beräkningsmetod som är baserad på tätshetsfunktionalteorin, för
vilken Walter Kohn belönades med Nobelpriset i kemi år 1998. I denna metod
löses Kohn-Sham-ekvationen, vilket ger den laddningstäthet som minimerar
de växelverkande elektronernas totala energi. Metoden som används för att
lösa denna ekvation i denna avhandling kallas full potential linear muffin-tin
orbital method (FP-LMTO). Det är en vidareutveckling av den vanliga
LMTO metoden, i vilken den potential som påverkar elektronerna antas vara
sfärisk runt atomerna. En fullpotentialmetod tar däremot hänsyn till den
verkliga, icke-sfäriska, potentialen. Metoden inkluderar även relativistiska
effekter, bland annat spinn-banväxelverkan, som ger upphov till den
magnetokristallina anisotropin.

Den magnetokristallina anisotropin låser magnetiseringen i en magnet i en
viss riktning i förhållande till kristallgittret, den så kallade lätta riktningen.
Den magnetokristallina anisotropienergin är energiskillnaden mellan denna
riktning och den hårda magnetiseringens riktningen och är ett mätt på hur svårt
det är att vrida magnetiseringen bort från den lätta riktningen. Vissa tekniska
tillämpningar kräver en liten magnetokristalllin anisotropi. Sådana magnetiskt
mjuka material används till exempel i transformatorer för att minska förlust-
terna och ingår även i läshuvudet i datorns härddisk. Material med en stor
magnetokristallina anisotropi kallas för magnetiskt hårda och används till ex-
emplar i permanentmagneter, men även för att lagra information i en härddisk,
där varje databit, en etta eller en nolla, lagras som en magnetiseringens riktning
i en liten volym. För att kunna lagra allt mer information på en given yta
har man alltsedan härddiskens uppkomst minsat denna volym. Detta kräver
i sin tur att den magnetokristallina anisotropienergin höjs för att förhindra att
magnetiseringen slumpmässigt byter riktning, en effekt som kallas superpara-
magnetism och leder till informationsförlust.

I denna avhandling studerades en rad magnetiska material, främst
med avseende på deras magnetokristallina anisotropi, men även deras
magnetisering, som är ytterligare en viktig parameter i tekniska sammanhang
och kan beskrivas som en magnets styrka. Den enaxliga magnetokristallina
anisotropin i tetragonala och trigonala kristallstrukturer av järn, kobolt
och nickel studerades som funktion av deformering från den kubiska
strukturen. Den magnetokristallina anisotropin ökar avsevärt när den kubiska
symmetrin bryts. Utifrån en analyser av järns och kobolts elektronstruktur
förutspåddes tetragonala legeringar av järn och kobolt som nya material med
e en ovanligt stor magnetokristallin anisotropi, något som bekräftades med
hjälp av första-princip-beräkningar samt experimentella studier på supergitter
upbyggda av lager av denna legering och platina. Ett material som är känt
för sin stora magnetokristallina anisotropi, vilken orsakas av platinas starka
spinn-banväxelverkan i kombination med den starka växelverkan mellan

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Finally, after almost six years, Ref. [119] of [45] is finished, with \( n = 5 \). It was a long journey and I couldn’t have done it without a number of people whom I’d like to thank here.

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