Diploma Thesis

Growth and Characterization of Ferromagnetic Heusler Compound Thin Films

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Chapter 1

Introduction

In the last three decades the miniaturization of electric circuits in electronic devices has rapidly developed. The aim is to produce smaller and more energy-efficient electronic elements with a higher performance than the former generation. That's why new techniques were established to shrink the size of electrical circuits. The current CPUs (central processor units) are fabricated in 45 nm technique - the first processor chips with 32 nm fabrication technique will be released in January 2011. More than ten years ago only nanoscale structures of 250 nm could be realized. However, it is predicted that the miniaturization process soon reaches its physical limits. In the past five years, for example, the clock frequencies of the processors could not be increased significantly anymore. Further performance improvements beyond the end of the semiconductor road-map appear neither technically nor economically feasible. Thus new concepts are necessary to grant an improvement of efficiency and performance in the field of semiconductor electronics.

Spin-electronic (spintronic) devices offer a replacement technology in which a spin degree of freedom is introduced into conventional electronics. Information could be encoded in the form of electron spin as well as charge.

The importance of this new research field was emphasized by awarding Albert Fert and Peter Grünberg 2007 with the Nobel prize in physics, for their discovery of the giant magnetoresistance effect (GMR) [1, 2]. The GMR was a milestone for the data storage in modern hard disk drives, which are equipped with GMR read heads which can very sensitively detect small magnetic fields. 1998, IBM was the first company which introduced hard disks based on the GMR granting them a commercial break-through.

For the development of hard disks, as well as for every new technology, a profound knowledge about the used material system and physical mechanisms is necessary. A key element for the realization of spintronic devices is the controlled manipulation of the magnetiza-
Chapter 1

Introduction

Magnetization $\mathbf{M}$, generally done by external magnetic fields. The magnetization of a ferromagnetic material is oriented alongside favorable crystallographic directions, the easy axes. The reason for this phenomenon, called magnetic anisotropy, are the differences in the free energy of the magnetization for different directions. By controlling this magnetic anisotropy which is influenced by the shape of the material, the crystalline structure and strain, the direction of the magnetization can be manipulated. Thus it is important to understand how and to what extent the physical parameters influence the magnetic anisotropy and which methods can be used to control them. A profound knowledge about the anisotropy is not only interesting for fundamental research, but can also be useful for technical applications which will benefit from fabricating self-tailored ferromagnetic materials with desired anisotropy parameters.

One material system in which we investigated the magnetic anisotropy are Heusler compounds. Discovered in the 1900s, but gained newly arising interest in 1983, band structure calculations revealed that some Heusler compounds are so called 'half metals' [3]. These half metals are theoretically 100% spin polarized. Due to their lattice constant matching with the III–V semiconductors, high Curie temperature $T_C$ above room temperature and large bandgap at the Fermi level in general, the Heusler alloys hold the greatest potential to realize the half-metallicity at room temperature among the half-metallic ferromagnets [4]. They are already used in spin-filters to inject a spin-polarized current into a semiconductor.

To measure the magnetic anisotropy there are different methods: the magneto-optic Kerr effect (MOKE), the superconducting quantum interference device (SQUID) magnetometry, the ferromagnetic resonance (FMR) and angle dependent magnetotransport measurements. We used the latter method which has the advantage to determine the magnetic anisotropy in micro-structures. It will be shown how the magnetic anisotropy can be determined quantitatively from a simulation fitting the experimental data.

In this thesis we investigated the magnetic anisotropy in two material systems by angle dependent magnetoresistance (ADMR) measurements: Heusler Co$_2$FeAl thin films, fabricated via magnetron sputtering at the university of Bielefeld, and (Ga,Mn)As thin films, fabricated by molecular beam epitaxy (MBE) at the university of Ulm. Co$_2$FeAl exhibits one of the highest magnetic moments ($4.9 \mu_B$ [5]) per formula unit and Curie temperature (1100 K [6]) among all half-metallic ferromagnets investigated so far. (Ga,Mn)As is a well known ferromagnetic semiconductor with a Curie temperature of about 100...200 K, depending on the doping concentration of manganese. With a new measurement setup we
additionally performed angle dependent magnetothermopower measurements (ADMTP) in these material systems, to analyze the magnetic anisotropy and thermopower. Hereby, instead of a current a temperature gradient generates a voltage potential which can be detected. Another goal of this diploma thesis was the fabrication and characterization of Heusler thin films grown via pulsed laser deposition (PLD). In the past 5 years first groups reported to have successfully grown high quality Heusler thin films by PLD [7, 8, 9, 10] which evoked our interest in growing Heusler thin films. The grown films were investigated by SQUID magnetometry, energy-dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD) measurements to get information about the magnetic and structural characteristics of the films.

In chapter 2 we give a brief introduction into the material class of Heusler compounds, including their composition, crystal structure and half metallicity. We present the free energy model used to describe the magnetic anisotropy with its various contributions and explain the ADMR measurement method experimentally. Afterwards the phenomenological theory behind the ADMR measurement for single-crystalline materials is discussed in detail: Starting from a series expansion of the resistivity tensor in powers of the magnetization and taking into account the crystal symmetry and Onsager relation, we derive equations for the longitudinal and transverse resistivity. These equations are used to simulate the measured ADMR data whereas the fitting parameters define the different resistivity and magnetic anisotropy parameters. We use the same phenomenological theory - slightly altered - to describe the Seebeck tensor and to simulate the measured ADMTP data.

In chapter 3 we present the ADMR measurements of four Co$_2$FeAl Heusler thin films of different thicknesses. The measurements were performed at various magnetic fields, temperatures and for three different rotation configurations of the external field $H$. We show that the simulation fits the data very well and discuss the obtained resistivity and anisotropy parameters.

In Chapter 4 the influence of magnetization orientation on thermopower is investigated via ADMTP measurements. To test our new measurement setup we start studying (Ga,Mn)As thin films first, since they exhibit a larger anisotropic magnetoresistance (AMR) in comparison to Co$_2$FeAl thin films, leading to higher thermoelectrical voltage signals. We then profoundly discuss the ADMTP measurement results for (Ga,Mn)As, and compare them with the results of the ADMR measurement also performed in this material system. The simulation of the ADMTP data via the Seebeck tensor model did
work very well, but we are going to argue whether the new Seebeck coefficient parameter $S_C$, which does not appear in the resistivity tensor model, is necessary for achieving good fitting results. For Co$_2$FeAl we detected a thermoelectrical voltage, but the signal was too weak to properly perform ADMTP measurements.

In chapter 5, the fabrication process of two Heusler targets, Co$_2$FeAl and Co$_2$MnSi for the PLD is described. We concentrated our efforts on the growth of Co$_2$MnSi thin films because a lot of groups reported on successfully having grown this Heusler compound by PLD (e.g. [7, 8, 11, 9]) and their growth parameters were a good reference and starting point for our own film growth. SQUID, EDX and XRD measurements yielded information about the magnetic and structural characteristics of the grown thin films. At the end we compare our Co$_2$MnSi films with those from the university of Bielefeld, grown by sputtering.

Chapter 6 summarizes the results of this thesis and an outlook presents ideas for further measurements and investigations.
Chapter 2

Theoretical Approach

In this chapter a brief introduction into the material class of Heusler compounds is given which evoked great interest in the last decade when band structure calculations showed that some Heusler compounds are half metallic ferromagnets [3]. They are promising candidates for spin injection into semiconductors due to their suited lattice parameters which match those of III-V semiconductors very well. This diploma thesis deals with angle dependent magnetoresistance (ADMR) and angle dependent magnetothermopower (ADMTP) measurements in these materials.

In chapter 2.2, we start from the free energy model to describe the different anisotropies and briefly address the important effects in the magnetotransport regime. Then, a detailed discussion about the resistivity tensor, the longitudinal and transverse resistivity calculated from the model and the integration of this phenomenological model into a simulation is given. This simulation is needed to fit the experimental data and to extract the important anisotropy and resistivity parameters.

In chapter 2.3, we discuss the Seebeck effect and the differences between the resistivity and the Seebeck tensor. With only little changes one can adopt the model of the resistivity tensor to the Seebeck tensor. We compare the terms of the longitudinal and transverse resistivities with the longitudinal and transverse Seebeck coefficients and conclude with the simulation of the Seebeck tensor.

2.1 Heusler Compounds

The discovery of the new material class of Heusler compounds goes back into the 1900s when the German mining engineer and chemist Friedrich Heusler found that Cu$_2$MnAl was ferromagnetic, even though it does not contain any pure ferromagnetic elements [12].
Since this discovery a large effort was put into the study of these new material systems with the composition $X_2YZ$, where $X$ (red) and $Y$ (blue) are transition metals and $Z$ (green) is a main group element (cf. Fig. 2.1a)).

![Figure 2.1: (a) Major combination of Heusler alloy formation (b) Curie temperatures of different full-Heusler compounds (both taken from [4])](image)

Furthermore a second material class was found with the composition $XYZ$, which showed the same behavior. The latter class was named half-Heusler whereas $X_2YZ$ is now known as full-Heusler compound. In 1983 the band structure of the half-Heusler NiMnSb was calculated by Groot et al. [3] and was named ‘half metal’ (not to be confused with a semi-metal). In these materials the spin separated band structure exhibits two different behaviors depending on the spin orientation: metallic for the majority spin band (i.e. the Fermi level lies within a band providing conduction electrons at the Fermi surface) and insulating for the minority spin band (Fermi level between conduction and valence band). This means that we have theoretically 100% spin polarized carriers in this material - the ‘density of states’ spin polarization is defined as [13]: $P = \frac{N_{\text{maj}} - N_{\text{min}}}{N_{\text{maj}} + N_{\text{min}}}$, where $N_{\text{maj}}$ is the density of states for the majority electrons and $N_{\text{min}}$ is the density of states for the minority electrons. This feature was crucial for the growing interest in spintronics research in the last decade, which goal is to generate, maintain and control highly spin polarized currents. Ab initio calculations revealed other half-metallic Heusler systems (see Fig. 2.2). In particular, the candidates with the structure $Co_2YZ$ were of enormous interest due to their high Curie temperatures (cf. Fig. 2.1b)). The origin of the bandgap

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1In a semi-metal (i.e. bismuth) there is a very small overlap between the bottom of the conduction band and the top of the valence band.
in the Heusler alloys is attributed to the strong d-band hybridization of the two transition metals X and Y.

![Figure 2.2: LDA (local-density approximation) calculations of the band structure of Co$_2$FeSi with (a) minority spin band (insulating behavior) and (c) majority spin band (metallic behavior). In (b) the density of states for the minority and majority carriers is shown. (figure taken from [14])](image)

At low temperatures a spin polarization of 50 - 60 % for Co$_2$FeAl and Co$_2$FeSi was experimentally found [15]. Due to their lattice constant matching with the III–V semiconductors, high Curie temperature $T_C$ above room temperature and large bandgap at the Fermi level in general, the Heusler alloys hold the greatest potential to realize the half-metallicity at room temperature among the half-metallic ferromagnets [4]. Current applications for Heusler compounds are magnetic tunnel junctions (MTJs) because of their large tunnel magnetoresistance (TMR) or spin-filters to inject a spin-polarized electron current into a semiconductor [4].

Full-Heusler compounds crystallize in the L$_{21}$ structure shown in Fig. 2.3(a) where the unit cell consists of four interpenetrating fcc sub-lattices. When we take Co$_2$FeAl as an example of a full Heusler compound, the positions of the two Co atoms are at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$, while the Fe atom is located at (0, 0, 0) and the Al atom at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Usually there is some disorder in the crystal structure which leads to an intermixing of the atoms. In the B2 structure (see Fig. 2.3(b)) the positions of Fe and Al atoms are mixed, in the DO$_3$ structure the Co and Fe atoms are intermixed and in the A2 structure all atoms can be at arbitrary positions within the crystal lattice. To obtain the totally ordered L$_{21}$ structure high annealing temperatures are usually required. To investigate the structural properties
there is a huge variety of methods, such as x-ray and neutron diffraction, anomalous x-ray diffraction, extended x-ray absorption fine structure (EXAFS) and nuclear magnetic resonance (NMR) [16]. In this work, we use x-ray diffraction to obtain information about the structural quality and surface roughness of the thin Heusler films investigated.

Other important properties of Heusler compounds that must be characterized and controlled are the magnetic anisotropy, magnetic exchange and damping. Magnetic anisotropies play an important role in determining the details of magnetization reversal, and affect important properties such as the coercive field and remanence. Especially for the mentioned applications above the quantitative knowledge of the magnetic anisotropy of Heusler compounds is crucial in order to systematically fabricate Heusler films of self-tailored anisotropy and control their switching behavior. The discussion of the magnetic anisotropy in the material system Co$_2$FeAl will be one of the main topics in this diploma.

**Figure 2.3:** Different ordered structures of full-Heusler compounds: (a) L$_{21}$ structure (b) B2 structure (c) DO$_3$ structure (d) A2 structure [16]
2.2 Theory of Angle Dependent Magnetoresistance (ADMR)

In this section the theoretical fundament of the ADMR measurement is presented. We are starting with the free energy model which can be used to describe the magnetic anisotropy. After that the magnetotransport is briefly discussed along with its effects. Then the anisotropic magnetoresistance for polycrystalline and single crystalline samples is explained where the main attention is focused on the determination of the resistivity tensor. Afterwards the technique of ADMR is presented together with the three different rotation orientations we used for our experiments and the simulations are described. The latter are necessary to obtain all the resistivity and anisotropy parameters when the experimental data is fitted by the simulation. The simulation minimizes the free energy and calculates the longitudinal and transverse resistivity which can directly be compared to the measured values. At last some simulation examples for different fields and crystal symmetries are given.

2.2.1 Magnetic Anisotropy

Before we start with the explanation of the magnetic anisotropy a nomenclature for vectors is introduced. As an example for the nomenclature we take the vector of the magnetization \( \mathbf{M} \). \( \mathbf{M} \) can be separated into \( M \mathbf{m} \) where \( M \) is the absolute value of the magnetization and \( \mathbf{m} \) is the unit vector of the direction of the magnetization. The components of \( \mathbf{m} \) are \( m_i, i \in \{x, y, z\} \). For all vectors in this diploma thesis like the current density or magnetic field we will use this nomenclature.

For ferromagnetic samples the magnetization \( \mathbf{M} \) does not have to be oriented in the direction of the external magnetic field \( \mathbf{H} \). There can be energetically favorable (easy) and unfavorable (hard) directions for \( \mathbf{M} \). These anisotropies can be caused by the crystal symmetry, applied stress or the shape of the ferromagnet. These anisotropies can be described by the free energy \( F_{\text{tot}} \) model where the magnetization always points into the direction of minimal free energy. The free energy is normalized to the saturation magnetization \( F_{\text{tot},\mathbf{M}} = \frac{F_{\text{tot}}}{M} \) and includes the following terms [17]:
$$F_{\text{tot}, M} = F_{\text{stat}} + F_{\text{shape}} + F_{\text{aniso}} + F_{\text{magel}}$$ (2.1)

Here $F_{\text{stat}}$ is the Zeeman energy density, $F_{\text{shape}}$ is the shape anisotropy, $F_{\text{aniso}}$ is the anisotropy caused by the crystal symmetry and $F_{\text{magel}}$ is the magneto-elastic contribution to the free energy.

**Zeeman Energy**

The Zeeman energy density is the magneto-static energy density of the magnetization in an external field $H$ given by the following equation:

$$F_{\text{stat}} = -\mu_0 H \cdot m$$ (2.2)

For large external fields this contribution to the free energy dominates because this is the only term in which the external magnetic field $H$ plays a role.

**Shape Anisotropy**

The shape anisotropy represents the energy of the magnetization in a magnetic stray field. The magnetization $M$ orientates into the direction which minimizes the energy of the stray field. Here the geometry of the sample plays a crucial role. For example in our (001)-oriented thin film samples, the film plane is an easy plane for the magnetization and can be described by the equation:

$$F_{\text{shape}} = \frac{\mu_0}{2} M m_i^2$$ (2.3)

where $m_i, i \in \{x, y, z\}$ are the components of $m$ pointing in the directions [100], [010] or [001]. The shape anisotropy in the thin film shows an uniaxial anisotropy along the hard axis [001].

**Anisotropy due to the Crystal Symmetry**

The crystal symmetries in the samples cause a further contribution to the free energy. One distinguishes between two components of $F_{\text{aniso}}$, the uniaxial part $F_u$ and the cubic part $F_{\text{cub}}$. 
We use the convention of Chikazumi [18] to write the cubic anisotropy as:

\[ F_{\text{cub}} = B_{c1}(m_x^4 + m_y^4 + m_z^4) + B_{c2}(m_x^2m_y^2m_z^2) \]  

(2.5)

 Usually the term \( B_{c1} \) dominates the cubic anisotropy (\( |B_{c1}| \gg |B_{c2}| \)) and is of the fourth order leading to a four-fold symmetry with two easy axes. When the cubic symmetry of the crystal is altered by strain or other structural disorder an uniaxial anisotropy must be added (\( \mathbf{e} \) is the normalized unit vector in direction of the uniaxial anisotropy):

\[ F_{u} = B_u (\mathbf{e} \cdot \mathbf{m})^2 \]  

(2.6)

The sign of \( B_u \) decides if the anisotropy creates a hard axis (\( B_u > 0 \)) or an easy axis (\( B_u < 0 \)) along the direction of the unit vector.

**Magneto-elastic Anisotropy**

Caused by mechanical stress a magnetic anisotropy can be induced. This can be written as

\[
F_{\text{magel}} = -\frac{3}{2}\lambda_{100}\sigma \left( m_x^2\gamma_x^2 + m_y^2\gamma_y^2 + m_z^2\gamma_z^2 - \frac{1}{3} \right)
- 3\lambda_{111}\sigma \left( m_xm_y\gamma_x\gamma_y + m_ym_z\gamma_y\gamma_z + m_zm_x\gamma_z\gamma_x \right)
\]  

(2.7)

where \( \lambda_{100} \) and \( \lambda_{111} \) are the magneto-elastic constants in [100] and [111] direction, \( \sigma \) the stress and \( \gamma_i; i \in \{x,y,z\} \) the cosines of the stress pointing in the specified direction \( i \). Further information can be found in [18, 19].

**Free Energy for Full-Heusler Compounds**

For a Heusler thin film in the x-y-plane with its normal vector in [001] direction we can sum up the free energy as follows:
\[ F_{\text{tot,M}} = -\mu_0 H (\mathbf{h} \cdot \mathbf{m}) + B_{\text{cub}} (m_x^4 + m_y^4 + m_z^4) + \frac{1}{2} B_{110} (m_x + m_y)^2 + B_{001} m_z^2 \]  

(2.8)

The parameter \( B_{\text{cub}} \) reflects the cubic crystal symmetry of the Heusler compound, whereas the \textit{out-of-plane} uniaxial anisotropy parameter \( B_{001} \) is a combination of shape anisotropy (thin film) and strain (tetragonal distortion) hindering the magnetization to point towards the hard axis [001] direction. The origin of the uniaxial \textit{in-plane} \( B_{110} \) contribution is still under discussion [20, 21, 22, 23].

### 2.2.2 Magnetotransport

One main aspect of this diploma thesis is the measurement of the magnetic anisotropy by magnetotransport measurements. Therefore in a patterned Hall-bar the longitudinal voltage between two contact pads parallel to the current and the transverse voltage (perpendicular to the current flow and between two opposite contact pads) are measured (see chapter 3.2 for further details on the experimental setup). The effect causing the transverse voltage is called Hall-effect and will be discussed in the next paragraph.

#### 2.2.2.1 Hall Effect

When there is a current flow through a conducting material and a component of the magnetic field is applied in a direction perpendicular to the current flow, the Lorentz force deflects the electrons into the direction perpendicular to the current and magnetic field. Thus a transverse voltage is built up and an electrical field is generated. This is the ordinary Hall-effect (OHE) in a one band model [13]:

\[ E_H = \frac{e\tau}{m} B_\perp J \]  

(2.9)

Here \( \tau \) is the scattering time, \( m \) the effective mass of the free electrons, \( J \) the electrical current density, \( e \) the elementary charge and \( \rho_0 \) is a constant specific resistivity parameter.

The Hall-coefficient \( R_H \) is defined as

\[ R_H = \frac{E_H}{B J} = \frac{1}{n e} \]  

(2.10)
and the transverse resistivity is given by:

$$\rho_{\text{trans}} = R_H \mu_0 H_\perp$$  \hspace{1cm} (2.11)$$

In these equations, $n$ is the charge density, $\mu_0$ is the vacuum permeability and $H_\perp$ is the component of the external magnetic field which points perpendicular to the film plane. According to Karplus and Luttinger [24] in ferromagnets there is an additional contribution to the transverse resistivity by the anomalous Hall-effect (AHE) leading to:

$$\rho_{\text{trans}} = R_H \mu_0 H_\perp + R_A \mu_0 M(H)$$  \hspace{1cm} (2.12)$$

The first term is the OHE which is proportional to the external magnetic field $H$, while the second term is the AHE contribution proportional to the magnetization $M$. The reason for the AHE is the spin orbit coupling where two main mechanisms play a crucial role, the skew-scattering and the side-jump process. Explanation and further information about these two mechanisms can be found in [25] and [26]. A very detailed review article about the AHE was written by Nagaosa et al. [27]. Usually both mechanisms simultaneously occur in magnetic materials which leads to the following dependence of the anisotropy coefficient $R_A$:

$$R_A \propto a \rho_{\text{long}} + b \rho_{\text{long}}^2$$  \hspace{1cm} (2.13)$$

For out-of-plane measurements the OHE and AHE are the most important effects, but when the magnetic field $H$ has no out-of-plane component and lies in-plane the predominant effect is the anisotropic magnetoresistance (AMR) which will be discussed in the next subsection.

### 2.2.2.2 Anisotropic Magnetoresistance (AMR)

In ferromagnetic materials the resistances $\rho_\parallel$ parallel and $\rho_\perp$ perpendicular to the orientation of the magnetization are different due to the spin orbit interaction. This effect is called the anisotropic magnetoresistance. The resistance is dependent on the angle between the magnetization and the current density $J$. If we now consider a thin film where
the magnetization lies in-plane and use Ohm’s law \[28\), \(E = \bar{\rho}J\), where \(E\) is the electrical field and \(\bar{\rho}\) is the resistivity tensor, we get

\[
\begin{pmatrix}
E_{\parallel} \\
E_{\perp}
\end{pmatrix} = \begin{pmatrix}
\rho_{\parallel} & 0 \\
0 & \rho_{\perp}
\end{pmatrix}
\begin{pmatrix}
J_{\parallel} \\
J_{\perp}
\end{pmatrix}.
\]

(2.14)

In this equation the parallel and perpendicular indices refer to the orientation of the magnetization. Since \(\rho_{\parallel} \neq \rho_{\perp}\), the resistivity tensor is not diagonal anymore in the x-y coordinate system, leading to

\[
\begin{pmatrix}
E_x \\
E_y
\end{pmatrix} = \begin{pmatrix}
+\rho_{xx} & -\rho_{xy} \\
+\rho_{xy} & +\rho_{yy}
\end{pmatrix}
\begin{pmatrix}
J_x \\
J_y
\end{pmatrix}.
\]

(2.15)

Now the off diagonal terms are not zero anymore and contribute to the electrical field by adding a term transverse to the current direction. This phenomenon is called planar Hall-effect (PHE) but should not be confused with the other ‘real’ Hall-effects discussed above, which are antisymmetric with respect to \(H\)- and \(M\)-inversion.

\[\text{Figure 2.4: Coordinate system for the AMR}\]

If \(\textbf{M}\) is pointing in an arbitrary direction in the film plane (cf. fig. 2.4), we get the following equation:
\[ E = \rho_\perp (J - (\mathbf{m} \cdot J) \mathbf{m}) + \rho_\parallel (\mathbf{m} \cdot J) \mathbf{m}. \]  

(2.16)

Assuming the current flowing in the x-direction and using \((\mathbf{m} \cdot J) = J \cos \theta\) and \(\mathbf{m} = (\cos \theta, \sin \theta, 0)\) we end up with

\[ \rho_{\text{long}} = \rho_\perp + (\rho_\parallel - \rho_\perp) \cdot \cos^2 \theta \]  

(2.17)

\[ \rho_{\text{trans}} = (\rho_\parallel - \rho_\perp) \cdot \sin \theta \cos \theta, \]  

(2.18)

where \(\theta\) is the angle between the magnetization \(\mathbf{M}\) and current direction \(\mathbf{J}\). This simplified model is only valid for polycrystalline samples. A model for single crystalline samples is introduced in the next chapter.

### 2.2.2.3 Resistivity Tensor for Single Crystalline Samples

Going to a single crystalline sample we have to take into account the crystal symmetry, which reduces the symmetry of the system. Now not only the angle between the magnetization \(\mathbf{M}\) and the current direction \(\mathbf{j}\) is important, but the orientation with respect to the different crystal axes of the sample. Therefore a new ansatz is needed. Following in the steps of R. R. Birss [29] and T. R. Mc Guire & R. I. Potter [30], who were one of the first using the phenomenological model describing the resistivity tensor, P. K. Muduli *et al.* used this model to describe the cubic \(\text{m}3\text{m}\) crystal symmetry of his Fe\(_3\)Si samples. This ansatz was also pursued by W. Limmer *et al.* [31] who studied single crystalline (Ga,Mn)As samples and extended this phenomenological approach by calculating the resistivity tensor for tetragonal systems. Limmer *et al.* also discussed different current directions and crystal planes in their paper. This method is now discussed, but not to the full extend. For further and more detailed information, see [31, 19, 32].

First we introduce some unit vectors: \(\mathbf{j}\) is the unit vector of the current density, \(\mathbf{n}\) the unit vector normal to the film plane and \(\mathbf{t}\) is the one in-plane perpendicular to the current direction \((\mathbf{t} = \mathbf{n} \times \mathbf{j})\). The coordinate system is chosen this way that the x,y,z-axes are pointing into the \([100],[010],[001]\) direction, respectively. Beginning with Ohm’s law (page 14) one can write the longitudinal and transverse resistivity as:
\[ \rho_{\text{long}} = \frac{E_{\text{long}}}{J} = \vec{j} \cdot \vec{\rho} \cdot \vec{j} \] (2.19)

\[ \rho_{\text{trans}} = \frac{E_{\text{trans}}}{J} = \vec{t} \cdot \vec{\rho} \cdot \vec{j}. \] (2.20)

The resistivity tensor can now be Taylor expanded in powers of the magnetization \( m_i; i \in \{ x, y, z \} \), resulting in

\[ \rho_{ij}(\vec{m}) = a_{ij} + a_{kij} \cdot m_k + a_{klmij} \cdot m_k m_l m_m + \ldots \] (2.21)

Neumann’s principle [33] implies that the tensor must reflect the intrinsic crystal symmetry, the same applies for the expansion coefficients \( a_{ij} \) which are defined as:

\[ a_{ij} = S_{io} S_{jp} \cdot a_{op} \]
\[ a_{kij} = |\vec{S}| S_{kq} S_{io} S_{jp} \cdot a_{qop} \]
\[ a_{klmij} = |\vec{S}|^2 S_{kq} S_{lr} S_{io} S_{jp} \cdot a_{qrop} \]
\[ \vdots \]

(2.22)

Note that for the equations (2.21) and (2.22) Einstein’s summation convention has to be applied. \(|\vec{S}|\) is the determinant of the symmetry matrix \( \vec{S} \) with its components \( S_{ij} \). There are multiple options in defining these symmetry generation matrices which contain the crystal symmetry. We use R. R. Birss [29] choice of the matrices, who described the different crystal symmetries with as few matrices as possible. Instead of the cubic symmetry of bulk Heusler crystals, we have to use a tetragonal symmetry for our Heusler thin films because of the shape of the film and tetragonal distortion due to epitaxial strain growth direction. For the tetragonal symmetry \( \vec{S}_2 \) and \( \vec{S}_8 \) of the nine generating matrices, for a cubic symmetry \( \vec{S}_2 \) and \( \vec{S}_9 \) are needed (cf. R. R. Birss page 48-49 [29]):

\[ \vec{S}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \vec{S}_8 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \]
Using the equations (2.22) up to the fourth order for both symmetry matrices $\bar{S}_2$ and $\bar{S}_8$ leads to ten equations where dependences between the $a_{ij}, a_{kij}, \ldots$ parameters can be extracted. For this magnetotransport resistivity tensor the Onsager relation [34] $\rho_{ij}(M) = \rho_{ji}(-M)$ is valid and reduces the amount of free parameters. Furthermore, the magnetization is unchanged by a permutation of the directions $m_x, m_y, m_z$, i.e. $m_x \cdot m_y = m_y \cdot m_x$, since a multiplication of scalars is interchangeable. With all these simplifications and by introducing new coefficients $A, B, C_1, C_2, a, b, c_1, c_2, c_3, \ldots, e_6$, which are linear combinations of the $a_{ij}, a_{kij}, \ldots$ parameters, we can finally write the resistivity tensor as

$$
\rho_{\text{tetragonal}} = \rho_{\text{cubic}} + \Delta \bar{\rho}
$$

with the terms in ascending powers of $m_x, m_y$ and $m_z$ [35]:

---

$^2$the parameters can be looked up in [35]
\[
\rho_{\text{cubic}} = A \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + B \begin{pmatrix} 0 & m_z & -m_y \\ -m_z & 0 & m_x \\ m_y & -m_x & 0 \end{pmatrix} + C_1 \begin{pmatrix} m_x^2 & 0 & 0 \\ 0 & m_y^2 & 0 \\ 0 & 0 & m_z^2 \end{pmatrix} \\
+ C_2 \begin{pmatrix} 0 & m_x m_y & m_x m_z \\ m_x m_y & 0 & m_y m_z \\ m_x m_z & m_y m_z & 0 \end{pmatrix} + D \begin{pmatrix} 0 & m_y^3 & -m_z^3 \\ -m_y^3 & 0 & m_x^3 \\ m_x^3 & -m_z^3 & 0 \end{pmatrix} \\
+ E_1 \begin{pmatrix} m_x^4 & 0 & 0 \\ 0 & m_y^4 & 0 \\ 0 & 0 & m_z^4 \end{pmatrix} + E_2 \begin{pmatrix} m_y^2 m_z^2 & 0 & 0 \\ 0 & m_x^2 m_z^2 & 0 \\ 0 & 0 & m_x^2 m_y^2 \end{pmatrix} \\
+ E_3 \begin{pmatrix} 0 & m_x m_y m_z^2 & m_x m_y^2 m_z \\ m_x m_y m_z^2 & 0 & m_x^2 m_y m_z \\ m_x^2 m_y m_z & m_x^2 m_y m_z & 0 \end{pmatrix}
\]

\[
\Delta \bar{\rho} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & a & 0 \end{pmatrix} + \begin{pmatrix} 0 & b m_x & 0 \\ -b m_z & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} c_3 m_x^2 & 0 & c_2 m_x m_y \\ 0 & c_3 m_y^2 & c_2 m_y m_z \\ c_2 m_x m_z & c_2 m_y m_z & c_1 m_z^2 \end{pmatrix} \\
+ \begin{pmatrix} 0 & d_1 m_x^3 & -d_2 m_y m_z^2 \\ -d_1 m_z^3 & 0 & d_2 m_x m_y^2 \\ d_2 m_x m_y^2 & -d_2 m_x m_y^2 & 0 \end{pmatrix} + \begin{pmatrix} e_2 m_y^2 m_z^2 + e_4 m_y^4 & e_3 m_x m_y m_z^2 & e_6 m_x m_y^2 m_z + e_7 m_x m_z^3 \\ e_3 m_x m_y m_z^2 & e_2 m_x^2 m_y^2 + e_4 m_x^4 & e_6 m_x m_y^2 m_z + e_7 m_y m_z^3 \\ e_6 m_x m_y m_z^2 + e_7 m_x m_z^3 & e_6 m_x^2 m_y m_z + e_7 m_y m_z^3 & e_5 m_y^2 m_z^2 + e_1 m_z^4 \end{pmatrix}
\]

(2.24)

(2.25)

The identity \( |m|^2 = m_x^2 + m_y^2 + m_z^2 \) was also used to simplify the resistivity tensor. With the help of some algebraic transformations and the vectors \( \mathbf{j} \| (1, 1, 0) \), \( \mathbf{n} \| (0, 0, 1) \) and \( \mathbf{t} \| (-1, 1, 0)^3 \) describing the film, we can now calculate \( \rho_{\text{long}} \) and \( \rho_{\text{trans}} \). To simplify the expression new parameters \( \rho_0, \rho_1, \ldots, \rho_9 \) (see Limmer et al. [35]) and the identities \( m_x = \frac{1}{\sqrt{2}} (\mathbf{j} \cdot \mathbf{m} - \mathbf{t} \cdot \mathbf{m}) \), \( m_y = \frac{1}{\sqrt{2}} (\mathbf{j} \cdot \mathbf{m} + \mathbf{t} \cdot \mathbf{m}) \), \( m_z = (\mathbf{n} \cdot \mathbf{m}) \) are used. Starting from the equations (2.19) and (2.20) and plugging in the tetragonal resistivity tensor \( \rho_{\text{tetragonal}} \) (2.23) we get for the resistivities:

\(^{3}\text{growth of the Heusler films is 45° rotated in respect to the substrate (see chapter 3.1)}\)
\[ \rho_{\text{long}} = \rho_0 + \rho_1 (\mathbf{j} \cdot \mathbf{m})^2 + \rho_2 (\mathbf{n} \cdot \mathbf{m})^2 + \rho_3 (\mathbf{j} \cdot \mathbf{m})^4 + \rho_4 (\mathbf{n} \cdot \mathbf{m})^4 + \rho_5 (\mathbf{j} \cdot \mathbf{m})^2 (\mathbf{n} \cdot \mathbf{m})^2 \] (2.26)

\[ \rho_{\text{trans}} = \rho_6 (\mathbf{n} \cdot \mathbf{m}) + \rho_7 (\mathbf{j} \cdot \mathbf{m})(\mathbf{t} \cdot \mathbf{m}) + \rho_8 (\mathbf{n} \cdot \mathbf{m})^3 + \rho_9 (\mathbf{j} \cdot \mathbf{m})(\mathbf{t} \cdot \mathbf{m})(\mathbf{n} \cdot \mathbf{m})^2 \] (2.27)

These are the resistivities with terms up to the fourth order of magnetization for a tetragonal symmetry which we need for our ADMR experiments with Heusler compounds. The terms \((\mathbf{j} \cdot \mathbf{m})\) and \((\mathbf{t} \cdot \mathbf{m})\) describe the in-plane dependencies of the resistivities, whereas \((\mathbf{n} \cdot \mathbf{m})\) adds an out-of-plane component. The AMR is found in the \(\rho_1\) and \(\rho_3\) parameters in the longitudinal resistivity, the AHE in the \(\rho_7\) and \(\rho_8\) parameters in the transverse resistivity and the PHE in the \(\rho_7\) parameter. In the simulation chapter 2.2.3.2 several different configurations of crystal symmetry and the influence of rotation geometry on the resistivities will be discussed.

### 2.2.3 Angle Dependent Magnetoresistance (ADMR)

The main part of this thesis reports on the angle dependent magnetotransport measurements (ADMR) in Heusler samples in order to quantitatively determine the anisotropy parameters. Commonly the ferromagnetic resonance (FMR) method is used for this purpose. However, comparing measurements to determine the anisotropy parameters of (Ga,Mn)As by Limmer et al. showed that the values for the anisotropy parameters obtained from FMR and ADMR measurements are the same [31].

In this chapter we will first give a short description of the measurement setup and technique (further details are discussed in chapter 3.2), then we proceed to the numerical simulation which we use to fit the acquired data and to extract the resistivity and anisotropy parameters. The simulation is based on Limmer et al. [31] and yields quantitative values for the anisotropy parameters. The implementation of the simulation into LabVIEW has been done by Matthias Althammer.

#### 2.2.3.1 Measurement Setup and Techniques

The measurements were performed in a cryostat which could be cooled down to 3K and in which a maximum magnetic field of \(\pm 7\) T could be generated. The thin film samples are patterned into Hall-bars, contacted on a chip carrier and mounted on a dipstick which is inserted into the cryostat (more detailed information can be found in the
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For the ADMR measurement the longitudinal and transverse voltages are measured at constant temperature and magnetic field $\mu_0H_{\text{measure}}$ while the dipstick is rotated. Before the measurement is started a predefined starting position must be established and a high magnetic field must be applied first before going down to $\mu_0H_{\text{measure}}$ in order to guarantee the same starting orientation for the magnetization. The measurement has been done at different temperatures in order to analyze the influence of temperature on the anisotropy and resistivity parameters and also at different magnetic fields to be able to determine the parameters. At high magnetic fields the magnetization of the sample is parallel to the external magnetic field, so that the anisotropy parameters have no influence on the behavior of the magnetization. In this way only the resistivity parameters matter for the high field case and can be determined. At low magnetic fields the magnetic anisotropy with its easy and hard axes comes into play and changes the behavior of the magnetization. Therefore at low fields the magnetic anisotropy parameters can be extracted. However there is a limit of the low field value because under a certain value the single magnetic domain of the sample decomposes into smaller domains and the single domain model used for the simulation is no longer valid. Signs of the decomposition of the domains can be found in the low field ADMR experiments in the $oopj$ geometry (explanation in Fig. 2.5).

To determine all resistivity and anisotropy parameters in the simulation, measurements in three orthogonal rotation planes are needed. In Fig. 2.5(a) we see the in-plane rotation of the external magnetic field $\mathbf{H}$ starting from the $[1\overline{1}0]$ direction and going counterclockwise to the $[110]$ direction and further on. In Fig. 2.5(b) and (c), the out-of-plane rotation orientations are shown. In the $oopj$ configuration the $\mathbf{j}$-vector and in the $oopt$ configuration the $\mathbf{t}$-vector, which lies in-plane perpendicular to the current direction, is parallel to the rotation axis. The angle $\varphi$ is the angle between the starting direction - $[1\overline{1}0]$ in the $ip$ and $oopj$ configuration, $[001]$ in the $oopt$ configuration - and the external magnetic field $\mathbf{H}$.
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Figure 2.5: Sketch of the three different rotation geometries: (a) in-plane rotation with normal vector \( n \) as rotation axis, (b) out-of-plane rotation with current density \( j \) as rotation axis, (c) out-of-plane rotation with the \( t \)-vector as rotation axis. In blue color the rotation angle \( \varphi \) is shown.

2.2.3.2 Simulation

In order to fit the measurement data a numerical simulation program was written in LabVIEW. The idea behind this simulation is to fit the measured longitudinal and transverse resistivity by choosing suitable values for the anisotropy and resistivity parameters.

The first step executed by the program is the minimization of the free energy by finding its global minimum, assuming that the magnetization points always into this direction (cf. chapter 2.2.1). The free energy is given by (cf. page 11)

\[
F_{\text{tot},M} = -\mu_0 H (h \cdot m) + B_{\text{cub}} (m_x^4 + m_y^4 + m_z^4) + \frac{1}{2} B_{110} (m_x \cdot m_y)^2 + B_{001} m_z^2. \tag{2.28}
\]

Knowing the direction of the magnetization, the longitudinal and transverse resistivities can be calculated. For the simulation it turns out that going up to the second order in magnetization is sufficient to get very good results for fitting the resistivities of the Heusler compounds (see chapter 3.4).

\[
\rho_{\text{long}} = \rho_0 + \rho_1 (j \cdot m)^2 + \rho_2 (n \cdot m)^2 \tag{2.29}
\]

\[
\rho_{\text{trans}} = \rho_6 (n \cdot m) + \rho_7 (t \cdot m) (j \cdot m) \tag{2.30}
\]

The only input required for the simulation are the parameters \( B_{\text{cub}}, B_{110}, B_{001}, \rho_0, \rho_1, \rho_2, \rho_6, \rho_7 \) which have to be deduced from the measurement data. This can be done as follows:

1. Typical anisotropy parameters \( B_{\text{cub}}, B_{110}, B_{001} \) for the material are chosen. \( B_{001} \)
should be at a high value so that the magnetic anisotropy lies *in-plane*.

2. For high fields \((\mu_0 H_{\text{measure}} \geq B_{\text{aniso}})\) the resistivity parameters \(\rho_i\) can be determined since the magnetization follows the external \(H\)-field and therefore the influence of the anisotropy parameters on the simulation is minimal. It is useful to start with the \(ip\) measurement because the *out-of-plane* terms in equation (2.29) and (2.30) are zero: \((n \cdot m) = 0\). Then, for the longitudinal fit only the constant factor \(\rho_0\), the offset, and the \(\rho_1\) parameter, determining the amplitude of the measurement curve, have to be adjusted such that they fit the data points. The same is done for the transverse resistivity.

3. For low fields \((\mu_0 H_{\text{measure}} = B_{\text{aniso}})\) the anisotropy is no longer negligible and \(B_{\text{cub}}\) and \(B_{110}\) can be determined for the \(ip\) configuration.

4. For all field measurements at a given temperature all anisotropy and resistivity parameters are constant, except \(\rho_0\) which has to be adjusted anew for each \(H\)-field. All parameters can be checked and slightly adjusted using the data of the measurements at other \(H\)-fields until one is satisfied with the \(ip\) fitting result.

5. After having successfully simulated the *in-plane* measurement, one can take a look at the two *out-of-plane* configurations. Only one *out-of-plane* geometry is needed to fit the rest of the parameters, which were zero in the \(ip\) configuration, because going to the second order of the magnetization is sufficient to get very good results for Heusler films. Again for high fields the resistivity parameters \(\rho_2\) and \(\rho_6\) can be found and for low fields \(B_{001}\) can be determined. The other \(oop\) configuration is used to verify all derived parameters.

In the next paragraph some didactic examples for different crystal symmetry and ADMR simulations of small and large H-fields are shown.

**Simulation Examples** First we analyze the difference of a cubic and tetragonal anisotropy in \(oopj\) geometry. In Fig. 2.6(a) we see the polar plot of the cubic crystal symmetry. Here, the dominant parts of \(\rho_{\text{long}}\) (see Eq. (2.26)) are plotted versus the angle \(\varphi\) (see Fig. 2.5 for details on rotation and geometry). In a polar plot, points on circles have the same values and going outwards means going to higher values. The blue resistivity curve shows clearly a fourfold symmetry, whereas the magenta curve in Fig. 2.6(b), which shows the tetragonal crystal symmetry, depicts a twofold symmetry. In both cases the
magnetic field was chosen high enough so that the influence of the anisotropy can not be seen. The cubic symmetry is four-leaved clover-shaped whereas the tetragonal symmetry is dumbbell-shaped. In the chapter 3.4, dealing with our experiments on Heusler compounds only tetragonal symmetry-shaped plots can be seen which verifies the tetragonal crystal symmetry of the Heusler films. The crucial part of equation (2.26) which is responsible for the cubic or respectively tetragonal crystal symmetry is given on top of each graph in figure 2.6.

\[
\begin{align*}
\rho_{\text{long}} &\propto (m \cdot n)^4 \\
\rho_{\text{long}} &\propto (m \cdot n)^2
\end{align*}
\]

(a) \( \varphi = 0^\circ [1-10] \)  
(b) \( \varphi = 0^\circ [1-10] \)

\[ \begin{array}{c}
\begin{array}{c}
330^\circ \\
300^\circ \\
270^\circ [00-1] \\
240^\circ \\
210^\circ \\
180^\circ [-110] \\
150^\circ \\
90^\circ [001] \\
60^\circ \\
30^\circ \\
0^\circ [001]
\end{array}
\end{array} \]

\[ \begin{array}{c}
\begin{array}{c}
330^\circ \\
300^\circ \\
270^\circ [00-1] \\
240^\circ \\
210^\circ \\
180^\circ [-110] \\
150^\circ \\
90^\circ [001] \\
60^\circ \\
30^\circ \\
0^\circ [001]
\end{array}
\end{array} \]

**Figure 2.6:** Longitudinal resistivity in oopj geometry for (a) cubic crystal symmetry and (b) tetragonal crystal symmetry. The equations on top of each graph show the term of (2.26) which is responsible for cubic or tetragonal crystal symmetry.

In the next comparison, we take a look at the \( \parallel \) longitudinal and transverse resistivities for small and large fields (see Fig. 2.7). The small field is represented in black whereas the large field is shown in red. The large field curve shows for both resistivities a dumbbell-shape which means that the magnetization is precisely following the external magnetic field. A changed behavior can be observed for the small field case where the anisotropy comes into play due to which the resistivity does not change gradually but abruptly at specific angles. The angles where those sudden changes occur are the hard axes and between those hard axes, easy axes can be found. In easy direction, the resistivity does not change until it is energetically more favorable for the magnetization to point in another
direction. This is caused by the rotation of the external magnetic field $H$ which changes the global minimum of the free energy, in which the magnetization is always pointing.

![Figure 2.7](image)

**Figure 2.7**: Small and large $H$-fields in $ip$ configuration for the (a) longitudinal resistivity (b) transverse resistivity. The orange lines indicate the easy axes, the green dashed lines the hard axes of the system.

These two examples were supposed to give only a brief insight into some important aspects of the simulation. In the diploma thesis of M. Wagner [32] a large amount of additional examples can be found dealing with the influence of the anisotropy and resistivity parameters on the plots and their shapes.
2.3 Theory of Angle Dependent Magnetothermopower (ADMTP)

In the last chapter the principles of ADMR and its simulation via the free energy model were discussed and presented as a tool to quantitatively determine the magnetic anisotropy of a ferromagnetic sample. In this chapter instead of driving an electric current through the Hall-bar we will drive a heat current through the sample by an applied temperature gradient resulting in a potential difference. Similar to the ADMR method we measure the longitudinal and transverse voltage and fit the measured data with a simulation to determine the anisotropy and resistivity parameters. Another goal is to analyze the differences between the resistivity tensor for the ADMR measurement and the Seebeck tensor for the ADMTP measurement.

2.3.1 Thermoelectrical Principles and Seebeck-effect

The physics of thermoelectrics have been developed mainly during two periods of strong activity in history. Thermoelectricity was first observed in 1821 by Seebeck [36]. From 1821 to 1851 the basic effects were discovered and understood macroscopically which were accompanied by applications in the fields of thermometry, power generation and refrigeration. In the next 80 years Altenkirch’s deviation of thermoelectric efficiency in 1911 [37] was the only important contribution to this field. In the late 1930s there began 20 years of progress leading to a microscopic understanding of thermoelectricity [36]. A resurgence of interest in thermoelectrics began in the mid 1990s when theoretical predictions suggested that thermoelectric efficiency could be greatly enhanced through nanostructural engineering, leading to experimental efforts to demonstrate the proof-of-principle and high-efficiency materials [38].

**Seebeck Effect**  When a temperature gradient is applied across a conducting material, an electric potential difference is induced. Known as the Seebeck effect, this phenomenon can be explained by treating the conduction electrons as particles. Since the kinetic energy of small particles increases with temperature, the electrons at the colder end of the conductor have less thermal energy than those at the hotter end. Therefore, on average more conduction electrons will move from hot to cold than from cold to hot. This net accumulation of electrons at the cold end gives a potential difference across the conductor. A schematic sketch of this effect can be seen in figure 2.8.
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Figure 2.8: Sketch of a conducting bar with a hot and a cold end which induce a current flow along the bar so that the cold end gets negative and the hot end positive. The temperature gradient lies along the [110] axis and the angle $\alpha$ is the angle between the \textbf{H}-field and the [110] axis. The longitudinal and transverse thermoelectrical (short therm.) voltages are measured as indicated in the sketch.

This Seebeck relation can be put into an equation where \textit{E} is the electrical field and, $\bar{\alpha}$ the Seebeck-coefficient and $\nabla T$ the temperature gradient:

$$E = -\bar{\alpha} \cdot \nabla T$$

In the most general form $\bar{\alpha}$ is a tensor like $\bar{\rho}$ in Ohm’s law (see chapter 2.2.2.2). The Seebeck-coefficient can also be written as $\alpha = -\frac{\Delta V}{\Delta T}$, where \textit{V} is the voltage.

\textbf{Nernst Effect}  The Nernst Effect can be explained similar to the Hall-effect (see 2.2.2.1): By applying a temperature gradient in x-direction and a magnetic field in z-direction an electrical field will be induced in y-direction. So instead of an electrical current here it is a heat current which is responsible for this effect.

Another phenomenon is the planar Nernst effect (PNE) which also contributes to the transverse electrical field. Here, there is still a temperature gradient in x-direction required but the magnetic field is lying \textit{in-plane} creating a electrical field in the y-direction. The name of the effect was chosen in respect to the planar Hall-effect (PHE, page 14) where instead of a temperature gradient, an electric potential gradient is applied. Both effects, the Nernst effect and the planar Nernst effect play an important role in the Seebeck tensor.
2.3.2 Calculation of the Seebeck Tensor

We now want to treat the Seebeck tensor in the same way as the resistivity tensor in chapter 2.2.2.3. Our goal is to perform angle dependent thermopower measurements and describe the data by a modified simulation using the Seebeck tensor instead of the resistivity tensor. So basically in spite of sending an electrical current by a sourcemeter through the sample, a thermal gradient is used to induce a static state in which a thermoelectric voltage can be measured across the bar.

Starting again with the series expansion, now for the Seebeck coefficient, we get the same equation:

\[
\alpha_{ij}(m) = s_{ij} + s_{kij} \cdot m_k + s_{klij} \cdot m_km_l + s_{klmij} \cdot m_km_lm_m + \ldots
\]  

(2.31)

Here the coefficients \(s_{ij}, s_{kij}, \ldots\) are defined analogous to equation (2.22) and the same generating matrices for the tetragonal symmetry were chosen. The difference between \(\bar{\alpha}\) and \(\bar{\rho}\) is that for the Seebeck-coefficient the Onsager relation does not lead to a reduction of expansion coefficients anymore [39]. As the Onsager relation only yields a relation between the Seebeck and Peltier tensor \(\pi_{ij}(M) = T\alpha_{ji}(-M)\), there are no further restrictions in symmetry for the Seebeck tensor and its expansion coefficients [40]. So only the restrictions due to commutation of the magnetization components \(m_k\) and crystal symmetry restrictions due to Neumann’s principle\(^4\) [33] remain. Therefore we get more independent coefficients when calculating the Seebeck tensor.

In table 2.1 an overview over the number of independent parameters for different applied symmetry operations is given up to the fourth order in magnetization. In the upper panel the case of cubic crystal symmetry is shown, in the lower panel always tetragonal crystal symmetry was applied. In the first row of both panels just Neumann’s principle and the crystal symmetry was taken into account. For the second rows Onsager’s relation \(\rho_{ij}(M) = \rho_{ji}(-M)\) [34] is used as well as the permutation of the magnetization directions \(m_x, m_y, m_z\), i.e. \(m_x \cdot m_y = m_y \cdot m_x\). With these symmetries the resistivity tensor \(\bar{\rho}\) is described. In the last rows the Onsager relation is not applied anymore, but the permutation of the magnetization directions is still allowed, which describes the case of the Seebeck tensor \(\bar{\alpha}\). We recognize that with increasing order of magnetization more and

\(^4\)The crystal symmetry is visible in all physical properties.
more additional parameters in the Seebeck tensor appear in comparison to the resistivity tensor. Already in the first order in tetragonal symmetry a change between both tensors can be detected whereas in the cubic symmetry one has to advance to the third order to see a difference.

Calculating the Seebeck tensor up to the fourth order in tetragonal symmetry, one receives:

\[
\alpha_{ij} = \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{pmatrix} + \begin{pmatrix} 0 & -B_3 m_y & B_4 m_y \\ B_1 m_z & 0 & -B_4 m_x \\ -B_2 m_y & B_3 m_x & 0 \end{pmatrix} + \begin{pmatrix} C_1 m_x^2 & 0 & 0 \\ 0 & C_1 m_y^2 & 0 \\ 0 & 0 & C_2 m_z^2 \end{pmatrix} \\
+ \begin{pmatrix} 0 & C_3 m_x m_y & C_6 m_x m_z \\ C_3 m_x m_y & 0 & C_6 m_y m_z \\ C_4 m_x m_z & C_4 m_y m_z & 0 \end{pmatrix} + \begin{pmatrix} 0 & C_7 m_z^2 & 0 \\ 0 & 0 & C_7 m_x^2 \\ 0 & 0 & 0 \end{pmatrix} \\
+ \begin{pmatrix} 0 & D_3 m_z^3 & -D_3 m_y^3 \\ -D_2 m_z^3 & 0 & D_4 m_x^3 \\ -D_2 m_z^3 & D_2 m_x^3 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -D_5 m_z^2 m_x & -D_7 m_y m_z \\ 0 & 0 & 0 \\ 0 & 0 & D_7 m_z m_x^2 \\ -D_6 m_z m_x m_y & 0 & -D_7 m_y m_z^2 \\
+ \begin{pmatrix} 0 & 0 & E_1 m_z^4 \\ 0 & 0 & E_1 m_y^4 \\ 0 & 0 & E_2 m_z^4 \\
+ \begin{pmatrix} E_3 m_y^2 m_z^2 & 0 & 0 \\ 0 & E_3 m_z^2 m_y^2 & 0 \\ 0 & 0 & E_4 m_z^2 m_y^2 \end{pmatrix} \begin{pmatrix} 0 & E_7 m_z m_x m_y & E_8 m_z m_y m_z \\ E_7 m_x m_y m_z & 0 & E_8 m_x m_z m_y \\ E_7 m_x m_z m_y & E_8 m_y m_z m_x & 0 \end{pmatrix} \\
+ \begin{pmatrix} E_9 m_z^4 & 0 & 0 \\ 0 & E_9 m_y^4 & 0 \\ 0 & 0 & E_9 m_z^4 \end{pmatrix} \begin{pmatrix} 0 & E_{10} m_z m_y & E_{12} m_z m_x \\ E_{10} m_x m_y & 0 & E_{12} m_y m_z \\ E_{10} m_y m_z & E_{11} m_z m_y & 0 \end{pmatrix} \right)
\]

(2.32)

In this equation we introduced new coefficients \(A_1, A_2, B_1, B_2, B_3, B_4, \ldots, E_{12}\) which are abbreviations for sums and differences of the series expansion parameters \(s_{ij}, s_{kl}, s_{klm}, s_{klnij} \; \forall \; k, l, m, i, j \in \{1, 2, 3\}\). These parameters can be found in the appendix A.1. To simplify Eq. (2.32) the identity \(m_x^2 + m_y^2 + m_z^2 = 1\) was used (for more details see page 104).

To compare resistivity with the Seebeck tensor, we use
\[ \alpha_{\text{long}} = \vec{j}_{\text{therm}} \cdot \vec{\alpha} \cdot \vec{j}_{\text{therm}} \]  
\[ \alpha_{\text{trans}} = \vec{t}_{\text{therm}} \cdot \vec{\alpha} \cdot \vec{j}_{\text{therm}} \]  

(2.33)  
(2.34)

to calculate the longitudinal and transverse component of the Seebeck tensor for a special geometry. Here \( \vec{j}_{\text{therm}} \) is the direction of the temperature gradient and \( \vec{t}_{\text{therm}} \) is the vector perpendicular to the \( \vec{j}_{\text{therm}} \) vector and to the normal vector \( \vec{n}_{\text{therm}} \) \( (\vec{t}_{\text{therm}} = \vec{n}_{\text{therm}} \times \vec{j}_{\text{therm}}) \).

We investigate the same case as we did for the resistivity tensor with the temperature gradient parallel to the [110] direction (it is the current direction in the resistivity case), the normal vector parallel to the [001] direction and the \( \vec{t}_{\text{therm}} \) vector parallel to the [\( \bar{1}10 \)] direction. Using the identities \( m_x = \frac{1}{\sqrt{2}}(\vec{j} \cdot \vec{m} - \vec{t} \cdot \vec{m}) \), \( m_y = \frac{1}{\sqrt{2}}(\vec{j} \cdot \vec{m} + \vec{t} \cdot \vec{m}) \), \( m_z = (\vec{n} \cdot \vec{m}) \) we get for the longitudinal and transverse component of the Seebeck coefficient:

\[ \alpha_{\text{long,110}} = S_0 + S_1(\vec{j} \cdot \vec{m})^2 + S_2(\vec{n} \cdot \vec{m})^2 + S_3(\vec{j} \cdot \vec{m})^4 + S_4(\vec{n} \cdot \vec{m})^4 + S_5(\vec{j} \cdot \vec{m})^2(\vec{n} \cdot \vec{m})^2 + S_A(\vec{j} \cdot \vec{m})(\vec{t} \cdot \vec{m})(\vec{n} \cdot \vec{m}) \]  
\[ \alpha_{\text{trans,110}} = S_6(\vec{n} \cdot \vec{m}) + S_7(\vec{j} \cdot \vec{m})(\vec{t} \cdot \vec{m}) + S_8(\vec{n} \cdot \vec{m})^3 + S_9(\vec{j} \cdot \vec{m})(\vec{t} \cdot \vec{m})(\vec{n} \cdot \vec{m})^2 + S_B(\vec{j} \cdot \vec{m})^2(\vec{n} \cdot \vec{m}) + S_C(\vec{j} \cdot \vec{m})^3(\vec{t} \cdot \vec{m}) \]  

(2.35)  
(2.36)

The \( S \)-parameters with numbers show that this term is already present in the longitudinal and transverse resistivity and \( S \)-parameters with letters indicate that these terms are new compared to the \( \rho_{\text{long, trans}} \) (the \( S \)-parameters can be looked up in the appendix (page 104)). Here the \( S_6 \) term can be identified with the Nernst effect and the parameter \( S_7 \) term as the PNE. The additional contributions to the Seebeck tensor with the parameters \( S_A \) and \( S_C \) are consisting of differences of the \( s_i; i \in \{1, 2, 3\} \) parameters, indicating that they might be very small, the exception is \( S_B \) which only consists of one term (cf. page 104). Thus for the simulation of the Seebeck measurements it will be very difficult to see the influence of the new parameters.
Table 2.1: Number of independent variables in the tensors when different symmetry operations are applied for the cubic (upper panel) and tetragonal (lower panel) crystal symmetry up to the fourth order of magnetization. In the first rows of both panels, just Neumann’s principles of crystal symmetry was taken into account, whereas in the second rows for the resistivity tensor, Onsager’s relation $\rho_{ij}(M) = \rho_{ji}(-M)$ and the permutation of magnetization (perm. of mag.) was included. For the Seebeck tensor this Onsager relation is not valid and leads thus to more independent variables in the tensor.

2.3.2.1 Simulation Examples

Due to our measurement setup for the Seebeck coefficient, it was only possible to conduct in-plane measurements (more information on the setup can be found in the experimental chapter 4.1). Our temperature gradient lies along the [110] axis in the zero position state when we insert the dipstick into the cryostat. Looking at equations (2.35) and (2.36) we see that there is only the $S_C$ parameter which has no out-of-plane contribution in the additional terms for the Seebeck coefficient. The terms with the factors $S_A$ and $S_B$ contain the oop contribution $(n \cdot m)$ which becomes zero in our $ip$ measurements. Hence it depends on the influence of the $S_C(j \cdot m)^3(t \cdot m)$ term if we can see any difference to the simulation model used for the resistivity tensor. As mentioned before $S_C = -4s_{212111} + 4s_{212221}$ contains a difference of the $s_i$ parameters and should be very small which could be verified in our experiments (see experimental chapter 4.2).

With the help of our simulation program we now simulate and illustrate the influence of the new Seebeck parameters. In Fig.2.9(a) we see the rotation angle $\varphi$ plotted versus the transverse thermo electrical voltage for an in-plane rotation. For this rotation configuration $(n \cdot m)$ becomes zero and thus only the terms with $S_T$ and $S_C$ survive from Eq. (2.36). The temperature gradient was set along the (110) axis. In the black curve the $S_C$ parameter is set zero whereas for the red curve this parameter is non zero. One clearly
recognizes a change of the dumbbell shape of the curve to a stretched dumbbell. In order to observe a clear difference we chose a slightly larger value for $S_C$ in comparison to $S_T$ ($S_T : S_C = 1 : 1.3$).

In our second example we want to investigate the influence of the Seebeck term $S_A (\mathbf{j} \cdot \mathbf{m}) (\mathbf{t} \cdot \mathbf{m}) (\mathbf{n} \cdot \mathbf{m})$ on the thermopower. To avoid that the term becomes zero we need a new rotation axis which is not parallel to any of the three vectors $\mathbf{j}$, $\mathbf{t}$ and $\mathbf{n}$. Thus we chose the diagonal axis (100) as the rotation axis and apply a temperature gradient in our standard direction (110). In the black curve the $S_A$ parameter is set zero, whereas in the red curve a non zero value for $S_A$ was applied (2.9(b)). To see a clear difference we chose the following ratio between the $S$-parameters: $S_A = S_1 = S_2 = 10 : 1 = S_3 = S_4 = S_5$ (cf. Eq. (2.35)). We observe that the red curve is no longer point symmetric with respect to the center and is stretched so that the new maxima are at an angle $\varphi$ of $125^\circ$ and $235^\circ$.

In the third and last example in Fig. 2.10 the influence of the Seebeck term $S_B (\mathbf{j} \cdot \mathbf{m})^2 (\mathbf{n} \cdot \mathbf{m})$ is studied. Again the diagonal (100) direction was chosen as rotation axis and the temperature gradient applied along (110) so that all terms in Eq. (2.36) remain. For the

**Figure 2.9:** (a) Simulation for an ip rotation where the rotation angle $\varphi$ is plotted versus the transverse thermoelectric voltage with (red) and without (black) the new Seebeck parameter $S_C$ (b) Simulation for an oop rotation with the diagonal (100) as rotation axis showing the influence of the $S_A$ parameter on the longitudinal thermoelectric voltage. The direction of the applied temperature gradient is (110) for both examples.
black curve, $S_B$ was set zero and in the red curve non zero. To see a clear difference we chose the following ratio between the $S$-parameters: $S_B = S_6 = S_7 = 10 : 1 = S_8 = S_9 = S_C$. We see that the red curve is larger than the black one showing a distinct bulge in the $\varphi = 0^\circ$ direction [001] which goes in the opposite direction for the black curve.

![Simulation for an oop rotation with the diagonal (100) as rotation axis showing the influence of the $S_B$ parameter on the transverse thermoelectric voltage. The direction of the applied temperature gradient is (110).](image)

**Figure 2.10:** Simulation for an *oop* rotation with the diagonal (100) as rotation axis showing the influence of the $S_B$ parameter on the transverse thermoelectric voltage. The direction of the applied temperature gradient is (110).

To really observe a different behavior in the experiment - if the coefficients are not too small to see anything - a new sample carrier system is needed for *out-of-plane* measurements in the cryostat. The new Seebeck parameter $S_B$ holds most promise to be detectable in the experiments because it is not consisting of a difference of $s_{ij}$ parameter but only $6s_{2321}$ (see appendix on page 104). Due to the ADMTP having been conducted in the last months of my diploma thesis there was not enough time left to realize this new setup for the dipstick head.
Chapter 3

Angle dependent Magnetoresistance

In this chapter we present angle dependent magnetoresistance (ADMR) measurements and compare the acquired data with our simulations. We have concentrated our studies on Co\textsubscript{2}FeAl because it is one of the most promising candidates for spintronic applications. This compound exhibits one of the highest magnetic moment (4.9 $\mu_B$ [5]) per formula unit (corresponding to an average value of 1.23 $\mu_B$ per atom) and Curie temperature (1100 K [6]) among all half-metallic ferromagnets investigated so far. We have investigated a series of films with thicknesses $d$ of 20, 50, 80 and 100 nm annealed at 500°C for one hour immediately after growth in-situ. In the published literature no quantitative value of the anisotropy parameters of Co\textsubscript{2}FeAl can be found, only the qualitative statement that there is a cubic and uniaxial anisotropy present which is quite low [41, 42, 43]. We extract these parameters from the simulation which fits the experimental data very well.

3.1 Preparation of the Heusler Samples

Growth of Co\textsubscript{2}FeAl The Heusler\textsuperscript{1} samples we used for our experiments were fabricated by I.-M. Imort at the university in Bielefeld via magnetron sputtering at room temperature. During the sputtering process a base pressure of $1 \cdot 10^{-7}$ mbar was maintained and the argon process pressure was about $1.5 \cdot 10^{-3}$ mbar. A 5 nm thick MgO buffer layer was deposited to cover the MgO (001) substrate and to coat surface contaminations [44]. Then, the Co\textsubscript{2}FeAl film was sputtered on the buffer layer. Its in-plane orientation is rotated by 45° with respect to MgO to guarantee a epitaxial growth and reduce the lattice mismatch. That means the (110) direction of the Co\textsubscript{2}FeAl film matches the (100) direction of the MgO substrate. From now on we only use the directions in the substrate

\textsuperscript{1}For further information on Heusler compounds see chapter 2.1
coordinate system as reference as indicated in Fig. 3.1. The lattice mismatch between the MgO buffer layer ($\sqrt{2} \cdot 4.21 \, \text{Å} = 5.95 \, \text{Å}$) and the Co$_2$FeAl compound (5.70 Å) is $\sim 4.5\%$ [44]. With x-ray reflectometry (XRR) the film thicknesses were determined. After the growth the Co$_2$FeAl films we investigated were annealed at 500°C for one hour in-situ. After the annealing process the Co$_2$FeAl films are present in the B2 structure [44] (see chapter 2.1 for details). In the ADMR experiment we investigated Co$_2$FeAl thin films with thicknesses $d$ of 20, 50, 80 and 100 nm. An overview of the samples, including their names, can be found in table 3.1.

<table>
<thead>
<tr>
<th>ID</th>
<th>Heusler material</th>
<th>film thickness</th>
<th>substrate</th>
<th>annealing procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFA12</td>
<td>Co$_2$FeAl</td>
<td>20 nm</td>
<td>MgO (001)</td>
<td>1 h @ 500°C</td>
</tr>
<tr>
<td>CFA7</td>
<td>Co$_2$FeAl</td>
<td>50 nm</td>
<td>MgO (001)</td>
<td>1 h @ 500°C</td>
</tr>
<tr>
<td>CFA8</td>
<td>Co$_2$FeAl</td>
<td>80 nm</td>
<td>MgO (001)</td>
<td>1 h @ 500°C</td>
</tr>
<tr>
<td>CFA9</td>
<td>Co$_2$FeAl</td>
<td>100 nm</td>
<td>MgO (001)</td>
<td>1 h @ 500°C</td>
</tr>
</tbody>
</table>

Table 3.1: Characteristic parameters of the four investigated Co$_2$FeAl Heusler films

**Hall-bar Patterning** The films were patterned into Hall-bars with a length of 900 μm and a width of 80 μm, using standard photolithography technique (cf. Fig. 3.2). The connection to the four contact pads on each side of the bar is 20 μm wide. On all four samples two Hall-bars were patterned, one parallel to the sample’s edges, so that the bar is along the [1-10] direction, and one 45° rotated, so that the bar is along the [100] direction (see Fig. 3.2). Thus, the magnetoresistance for current along different crystalline
orientations can be compared. However, in this thesis we focus onto the bar in [1-10] direction and only discuss this current direction.

**Chip Carrier Design** The Hall-bar samples were mounted onto home-made chip carriers as shown in Fig. 3.2(a). The sample hereby was glued onto a copper block using GE varnish [45], and the contact pads of the Hall-bars have been connected to the pads on the chip carrier PCB (printed circuit board) via 30µm thick Al wire bonds using the bonder K-1400 from Delvotec. By a short ultrasonic pulse the one end of the Al wire is bonded onto the contact pad of the Hall-bar and the other end onto a copper pad on the PCB. All five contact stripes on each of the four sides of the PCB are soldered to a 5 pin gold header. For ADMR experiments this whole sample carrier can be plugged in two different orientations into the dipstick head: (1) parallel to the dipstick, so that \( H \) is oriented perpendicular to the sample film plane and (2) perpendicular to the dipstick, so that \( H \) stays always in the sample film plane.

**Figure 3.2:** (a) A typical \( \text{Co}_2\text{FeAl} \) Hall-bar sample mounted into the home-made chip carrier. The two \( \text{Co}_2\text{FeAl} \) Hall-bars are wire bonded to the copper stripes on the PCB. (b) Microscope image of the used Hall-bar geometry, dimensions included

### 3.2 Measurement Setup and Geometry

**Measurement Setup** The dipstick is inserted into a superconducting split coil magnet cryostat (Oxford Instruments SM4000) in which a maximum magnetic field of ±7 T can be generated. The dipstick is situated inside the variable temperature insert (VTI) in the cryostat which can be cooled down to 2.4 K. Liquid helium is used for cooling and liquid nitrogen as a thermal shield to decrease the consumption of liquid He. CERNOX
temperature sensors and resistive heaters are positioned in the VTI as well as in the dipstick head. A Lakeshore 340 Temperature Controller is connected to the CERNOX temperature sensor and the resistive heater in the dipstick head whereas a Oxford Instruments ITC (intelligent temperature control) 503S controls the heater and reads out the temperature sensor in the VTI. Since the copper block, on which the Hall-bar samples have been glued, is thermally connected to the dipstick, the Lakeshore controller also sets the temperature on the sample. A stepping motor (OWIS DMT 100) is used to rotate the dipstick with respect to $\mathbf{H}$.

![Figure 3.3: Sketch of the Hall-bar showing the voltage probes and the applied current direction.](image)

**ADMR Measurement Technique** The ADMR measurements are performed at a constant applied field $\mathbf{H}$ and constant temperature. During the measurement, the magnetic field is rotated from -30° to 380° and back to -30° again in 2° steps so that there is a small overlap between forth and backsweep. That way, one can verify if the data at the angle $\varphi$ and $\varphi + 360°$ have the same value, i.e., if they are consistent. A current is applied across the Hall-bar by a Keithley K2400 sourcemeter and the longitudinal and transverse voltage are four-point measured by Keithley K2182 nanovoltmeters (cf. Fig. 3.3). This is done at each position of $\varphi$. Before starting the ADMR measurements a predefined starting position must be established and a high magnetic field ($2 - 3$ T) must be applied first before going down to $\mu_0 H_{\text{measure}}$, in order to guarantee the same starting orientation for the magnetization. LabVIEW-based software was used to control all the measurement devices mentioned above and for data acquisition.
ADMR Measurement Orientations  To determine all resistivity and anisotropy parameters in the simulation, measurements in three orthogonal rotation planes are needed. In Fig. 3.4(a) we see the *in-plane* rotation of the external magnetic field $\mathbf{H}$ starting from $\varphi = 0^\circ$ in the [1\bar{1}0] direction and rotating counterclockwise to the [110] direction ($\varphi = 90^\circ$) and further on. In Fig. 3.4(b) and (c) the *out-of-plane* rotation orientations are shown. In the oopj configuration the $\mathbf{j}$-vector and in the oopt configuration the $\mathbf{t}$-vector ($\mathbf{t} = \mathbf{n} \times \mathbf{j}$), which lies *in-plane* perpendicular to the current direction, is parallel to the rotation axis. The angle $\varphi$ is the angle between the starting direction - [1\bar{1}0] in the ip and oopj configuration, [001] in the oopt configuration - and the external magnetic field $\mathbf{H}$.

**Figure 3.4:** Sketch of the three ADMR measurement configurations: (a) *in-plane* rotation with normal vector $\mathbf{n}$ as rotation axis, (b) *out-of-plane* rotation with current density $\mathbf{j}$ as rotation axis, (c) *out-of-plane* rotation with the $\mathbf{t}$-vector ($\mathbf{t} = \mathbf{n} \times \mathbf{j}$) as rotation axis. In blue color the rotation angle $\varphi$ is shown, including its value at different rotation positions of $\mathbf{H}$.

### 3.3 A Characteristic Example

As a typical example for an ADMR measurement, we now discuss data taken from the 100 nm thick Co$_2$FeAl film at a temperature of 10 K in *in-plane* geometry at high external magnetic fields ($\mu_0 H = 2000 \text{ mT}$) and low fields ($\mu_0 H = 20 \text{ mT}$). In a common ADMR plot (Fig. 3.5) the longitudinal $\rho_{\text{long}}$ or transverse $\rho_{\text{trans}}$ resistivity is plotted versus the rotation angle $\varphi$ of the $\mathbf{H}$ field (cf. Fig. 3.4)). The resistivity is calculated from the measured voltages $V_{\text{long}}$ and $V_{\text{trans}}$ according to
\[
\rho_{\text{long}} = \frac{V_{\text{long}}}{I} \cdot \frac{b \cdot d}{l} \quad \rho_{\text{trans}} = \frac{V_{\text{trans}}}{I} \cdot d \tag{3.1}
\]

where \( b \) is the width and \( d \) the thickness of the Hall-bar and \( l \) is the distance between the contacts which measure \( V_{\text{long}} \). In Fig. 3.5(a) the data is displayed in a linear plot, whereas the same data is depicted in a polar plot in Fig. 3.5(b). The advantage of the polar plot is that symmetry aspects can be seen more easily. Therefore we are going to preferably use the representation of our data in polar plots.

![Figure 3.5: Longitudinal resistivity \( \rho_{\text{long}} \) of the 100 nm thick Co\(_2\)FeAl Heusler film, measured in in-plane geometry at 10 K. In black the \( \mu_0 H = 20 \text{ mT} \) and in red the \( \mu_0 H = 2000 \text{ mT} \) curves are depicted. (a) shows the conventional plot (b) the polar plot, in which the easy axes (orange) and hard axes (blue) are marked.](image)

At high magnetic fields the magnetization \( \mathbf{m} \) of the sample is parallel to the external magnetic field, so that no influence of the magnetic anisotropy can be observed. The AMR in our Heusler samples (see Sect. 2.2.2.2) leads to a maximum of the longitudinal resistivity when \( \mathbf{m} \) is perpendicular to the current density \( \mathbf{j} \) (\( \varphi = 0^\circ + n \cdot 180^\circ \)) and to a minimum when \( \mathbf{m} \) is parallel to \( \mathbf{j} \) (\( \varphi = 90^\circ + n \cdot 180^\circ \)), clearly visible in Fig. 3.5(a). Thus for Co\(_2\)FeAl thin films \( \rho_{\text{long}, \parallel} < \rho_{\text{long}, \perp} \) is valid (in contrast to metals where \( \rho_{\text{long}, \parallel} > \rho_{\text{long}, \perp} \)), which agrees with the observations of Vinzelberg \textit{et al.} in Fe\(_3\)Si [46]. At low magnetic...
fields (here $\mu_0 H = 20 \text{mT}$) the magnetic anisotropy with its easy and hard axes comes into play and change the behavior of the magnetization. The resistivity changes abruptly at some specific angles and on the other hand stays nearly constant in some angle sectors (cf. behavior of the black curves in Figs. 3.5(a) and (b)). The angles where those sudden changes occur are the hard axes (marked blue in Fig. 3.5(b)) and between those easy axes (marked orange in Fig. 3.5(b)) can be found. In easy direction, the resistivity does not change until it is energetically more favorable for the magnetization to point into another direction. This is caused by the rotation of the external magnetic field $\mathbf{H}$ which changes the global minimum of the free energy, in which the magnetization is always pointing.

For the majority of the measurements we measured the longitudinal voltage between two adjacent contact pads (for example 2 and 4 in Fig. 3.6(a)) which have a length difference of $l = 210 \mu\text{m}$ in respect to the Hall-bar. For the transverse resistivity $\rho_{\text{trans}}$ we measured the voltage between two opposing contact pads, for example 2 and 3 as depicted in Fig. 3.6(a). Since the connections from the Hall-bar to the contact pads ($20 \mu\text{m}$ width) could have a small offset, as exaggerated depicted in Fig. 3.6(a), an additional longitudinal part in transverse resistivity can be generated. This could be caused by the photolithography technique. Thus we have to subtract a certain percentage of the measured $\rho_{\text{long}}$ from $\rho_{\text{trans}}$ (always < 0.25%), so that in \textit{i}p configuration $\rho_{\text{trans}} = 0$ for $\mathbf{H} \parallel \mathbf{j}$ (cf. Eq. (3.6) where ($\mathbf{m} \cdot \mathbf{t}$) becomes zero and thus $\rho_{\text{trans}} = 0$). This would correspond to an offset of $l_{\text{offset}} = 0.53 \mu\text{m}$ for two opposite contact pads. In the transverse resistivity in Fig. 3.6(b) the original uncorrected scale is shown on the right side, whereas the corrected scale can be seen on the left side of the polar plot.

All in all, we investigated four Co$_2$FeAl thin films with thicknesses of 20 (CFA12), 50 (CFA7), 80 (CFA8) and 100 nm (CFA9) at $T = 10, 50, 100, 150, 200, 250, 300, 350 \text{K}$ and for magnetic fields of $\mu_0 H = 20, 40, 200, 500, 1000, 2000 \text{mT}$ in detail. An elaborate discussion of the $\rho_{\text{long}}(\varphi)$ and $\rho_{\text{trans}}(\varphi)$ plots follows in the next chapter, after the presentation of the fitting equations for the simulation.
Figure 3.6: (a) Exaggerated illustration of the longitudinal offset between the opposite numbered contact pads. We calculated a maximum offset of $l_{\text{offset}} = 0.53 \, \mu m$. (b) ADMR plot of $\rho_{\text{trans}}$ for the 100 nm thick Co$_2$FeAl Heusler film in in-plane geometry with (left scale) and without (left scale) offset correction at 10 K.

3.4 Experiment and Simulation

We now compare the ADMR data with the simulation based on the resistivity tensor model of R. R. Birss [29] and T. R. Mc Guire & R. I. Potter [30] (see Chpt. 2.2.2.3). In our simulation we fit the resistivity $\rho_i$ and anisotropy parameters $B_i$ so that the simulated curves for $\rho_{\text{long}}$ and $\rho_{\text{trans}}$ match the ADMR data. Hereby it is sufficient to go to the second order in the series expansion of the resistivity tensor to achieve good results in fitting the data of the Co$_2$FeAl films. Thus we are using Eqs. (2.29) and (2.30):

$$\rho_{\text{long}} = \rho_0 + \rho_1 (m \cdot j)^2 + \rho_2 (m \cdot n)^2$$

$$\rho_{\text{trans}} = \rho_{\text{offset}} + \rho_6 (m \cdot n) + \rho_7 (m \cdot j) (m \cdot t)$$

Here $\rho_{\text{offset}}$ is added ad hoc to the transverse resistivity equation (3.3) in order to correct the longitudinal offset between the bond contact points of the bond wires, as discussed in the previous chapter 3.3. For the further discussion this offset parameter will always be subtracted from $\rho_{\text{trans}}$, correcting the value of $\rho_{\text{trans}}$, and thus will not appear anymore in
the equation of $\rho_{\text{trans}}$. The magnetization orientation $\mathbf{m}$ can be calculated by minimizing the free energy (cf. Chpt. 2.2.1):

$$F_{\text{tot}, M} = -\mu_0 \mathbf{H} \cdot \mathbf{m} + B_{\text{cub}} (m_x^4 + m_y^4 + m_z^4) + \frac{1}{2} B_{110} (m_x + m_y)^2 + B_{001} m_z^2$$  (3.4)

For the simulation we fit the resistivity parameters $\rho_0, \rho_1, \rho_2, \rho_6, \rho_7$ and the anisotropy parameters $B_{\text{cub}}, B_{110}$ and $B_{001}$, so that the simulated curve matches the measured data. With the exception of $\rho_0$, the resistivity parameters were assumed to be field independent, which turned out to be a good approximation within the accuracy of the fit. As an example, the data and simulation of the 100 nm thick Co$_2$FeAl sample will be compared and discussed in the next chapter.

### 3.4.1 Discussion of the Experimental ADMR Data from the 100nm Thick Co$_2$FeAl Sample CFA9

In Figs. 3.7 and 3.9 the measured data (open squares) and simulation (lines) of the 100 nm thick Co$_2$FeAl sample CFA9 for all three ADMR measurement orientations are depicted. These measurements were performed at 10 K with an external magnetic field of $\mu_0 H = 20$ mT (black) and $\mu_0 H = 2000$ mT (red) applied. The current direction is along the [110] direction of the Hall-bar.

**Ip configuration** In *in-plane* configuration the *out-of-plane* components of Eqs. (3.2) and (3.3) are zero: $(\mathbf{m} \cdot \mathbf{n}) = 0$, reducing the equations to:

$$\rho_{\text{long}} = \rho_0 + \rho_1 (\mathbf{m} \cdot \mathbf{j})^2$$  (3.5)  
$$\rho_{\text{trans}} = \rho_7 (\mathbf{m} \cdot \mathbf{j}) (\mathbf{m} \cdot \mathbf{t})$$  (3.6)

The data of Fig.3.7(a) exhibit $\rho_{\text{long}} \sim (\mathbf{m} \cdot \mathbf{j})^2 \sim \cos^2 \varphi$ behavior for $\mu_0 H = 2000$ mT, as expected from Eq. (3.5). For $\varphi = 0^\circ + n \cdot 180^\circ$ the function $\cos^2 \varphi = 1$ and shows a maximum, whereas for $\varphi = 90^\circ + n \cdot 180^\circ$, we find a minimum ($\cos^2 \varphi = 0$). For the low field case ($\mu_0 H = 20$ mT) the magnetic anisotropy comes into play resulting in $\angle (\mathbf{j}, \mathbf{m}_{\text{ip}}) \neq \angle (\mathbf{j}, \mathbf{H}_{\text{ip}})$, i.e. the direction of the magnetization is not anymore always aligned parallel to the external magnetic field. Thus we get hard axes (at $\varphi \approx 36^\circ$ and $\varphi \approx 143^\circ$), where the resistivity changes abruptly, and easy axes in between (at $\varphi \approx 0^\circ$ and
\( \varphi \approx 90^\circ \), illustrated in Fig. (3.5)(b). This indicates that we have an \( ip \) cubic anisotropy. The simulation reproduces the measured data very well.

In Fig. 3.7(b) we see that the maxima and minima are shifted by 45° with respect to Fig. 3.7(a), where \( \rho_{\text{long}} \sim (\mathbf{m} \cdot \mathbf{j})^2 \sim \cos^2 \varphi \). As expected from Eq. (3.6), the transverse resistivity shows \( \rho_{\text{trans}} \sim (\mathbf{m} \cdot \mathbf{j})(\mathbf{m} \cdot \mathbf{t}) \sim -\cos \varphi \cdot \sin \varphi \) which exactly reproduces the data in Fig. 3.7(b): For \( \varphi = 135^\circ + n \cdot 180^\circ \) the function \( -\cos \varphi \cdot \sin \varphi = \frac{1}{2} \) shows a maximum, whereas for \( \varphi = 45^\circ + n \cdot 180^\circ \), we find a minimum \( -\cos \varphi \cdot \sin \varphi = -\frac{1}{2} \).

Due to the magnetic anisotropy, there is a small shift in the position of the maxima and minima for \( \mu_0 H = 20 \text{ mT} \) in comparison to the high field \( \mu_0 H = 2000 \text{ mT} \) measurement. An eye-catching point is the asymmetric behavior of the ADMR curves in Fig. 3.7(b) in respect to the origin, especially visible for the red curve (\( \mu_0 H = 2000 \text{ mT} \)). This is due to a misalignment of the sample out of the ideal flat position in the sample holder, as a simulation of a slightly changed rotation plane in Fig. 3.8 shows. In this figure the black curve shows the simulation of a perfect flat \( ip \) alignment of the sample with the film normal \( \mathbf{n} = (0, 0, 1) \), whereas the red curve depicts a simulation where the rotation axis is slightly tilted \( \mathbf{n}_T = (0.0055, -0.0145, 0.9999) \). Since the red curve fits the measured data very well, the sample must have been misaligned. The reason that such a small tilt angle leads to this tremendous change is the different magnitude of the \( \rho_6 \) parameter (anomalous Hall-effect) in comparison to the \( \rho_7 \) parameter (planar Hall-effect). Due to the tilted rotation plane, the \textit{out-of-plane} term \( \rho_6(\mathbf{m} \cdot \mathbf{n}) \) is no longer zero and since \( \rho_6 \) is about one order of magnitude higher than \( \rho_7 \), the new \( \rho_6 \) term has a significant influence on \( \rho_{\text{long}} \) (see Tab. 3.2, in which the fitting parameters for this sample are listed).
Figure 3.7: Simulation (lines) and data (open squares) of the 100 nm thick Co$_2$FeAl sample CFA9 at 10 K: (a) $\rho_{\text{long}}$ in $ip$, (b) $\rho_{\text{trans}}$ in $ip$, (c) $\rho_{\text{long}}$ in $oopj$ and (d) $\rho_{\text{trans}}$ in $oopj$ configuration for $\mu_0 H = 20$ mT (black) and $\mu_0 H = 2000$ mT (red).
**Figure 3.8:** A small misalignment of the sample (such that the film normal is not $n$, but $n_T$) leads to a significant asymmetry in the data points (open squares). While the original fit (black line), using $n$ as rotation vector, is not able to properly describe the data, the new simulation with $n_T$ (red line) as rotation vector reproduces the measured data very well.

### Oopj configuration

The ADMR data taken at 10 K in the *oopj* configuration is depicted in the panels (c) and (d) in Fig. 3.7. In this configuration $j$ is always perpendicular to the magnetization $m$, $(m \cdot j) = 0$, simplifying Eqs. (3.2) and (3.3) to:

\[
\rho_{\text{long}} = \rho_0 + \rho_2(m \cdot n)^2 \quad (3.7)
\]
\[
\rho_{\text{trans}} = \rho_6(m \cdot n) \quad (3.8)
\]

Figure 3.7(c) shows that $\rho_{\text{long}}$ is constant for $\mu_0 H = 20 \text{ mT}$ and $\mu_0 H = 2000 \text{ mT}$ in the *oopj* configuration, except for $\phi = 90^\circ$ and $\phi = 270^\circ$. For both of these angles the external magnetic field $H$ is perpendicular to the film plane and, if $\mu_0 H$ is large enough to overcome the uniaxial $B_{001}$ anisotropy, forces the magnetization into this direction. For our 100 nm Co$_2$FeAl sample the uniaxial *out-of-plane* anisotropy $B_{001} = 0.83 \text{ T}$ (cf. Tab. 3.2) is larger than the external magnetic field for the low field case $\mu_0 H = 20 \text{ mT}$. Thus the magnetic field is only for the high field case, $\mu_0 H = 2000 \text{ mT}$, strong enough...
to push the magnetization into the [001] or [00\bar{1}] direction. This results in a smaller value for $\rho_{\text{long}}$ for $\varphi = 90^\circ$ and $\varphi = 270^\circ$ because of the negative sign (cf. Tab. 3.2) of parameter $\rho_2$ in Eq. (3.7). For low fields ($\mu_0 H = 20\, \text{mT}$) a hysteresis in the measurement curve appears, which indicates the formation of magnetic domains, so that our ADMR macroscopic model is not applicable. Hence, our simulation fails to describe the measured data in the two angle sectors where the hysteresis effects occur.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
CFA 9 (100 nm) & 300 K & 150 K & 10 K \\
\hline
$\rho_0 (20\, \text{mT})$ [n\Omega m] & 737.15571 & 680.06714 & 645.33857 \\
$\rho_0 (2000\, \text{mT})$ [n\Omega m] & 736.70629 & 679.78114 & 645.13429 \\
$B_{\text{oo01}}$ [T] & 0.69 & 0.78 & 0.83 \\
$B_{\text{cub}}$ [T] & 0.003 & 0.004 & 0.0066 \\
$B_{\text{110}}$ [T] & -0.002 & -0.003 & -0.0035 \\
$\rho_1$ [n\Omega m] & -0.98429 & -1.09943 & -1.13657 \\
$\rho_2$ [n\Omega m] & -0.26 & -0.32314 & -0.33429 \\
$\rho_{\text{offset}}$ [n\Omega m] & 1.805 & 1.695 & 1.65 \\
$\rho_6$ [n\Omega m] & 8.3 & 7 & 7 \\
$\rho_7$ [n\Omega m] & -0.26 & -0.06 & 0.2 \\
\hline
\end{tabular}
\caption{Anisotropy and resistivity parameters used for fitting the 100nm thick Co$_2$FeAl sample CFA9 data listed for three different temperatures}
\end{table}

The $\rho_{\text{trans}}(\varphi)$ oop\textbf{j} data in Fig. 3.7(d) show that a magnetic field of $\mu_0 H = 20\, \text{mT}$ is not large enough to influence $\mathbf{m}$, leading to $\rho_{\text{trans}} = 0$ for all angles. For $\mu_0 H = 2000\, \text{mT}$ we observe a maximum at $\varphi = 90^\circ$ and a minimum at $\varphi = 270^\circ$. For $\varphi = 90^\circ$ the scalar product $(\mathbf{m} \cdot \mathbf{n})$ in $\rho_{\text{trans}}$ is positive (since $\mathbf{m} = \mathbf{h} = (0, 0, 1)$) and parameter $\rho_6$ as well (cf. Tab. 3.2), leading to the maximum value for $\rho_{\text{trans}}$. The opposite is the case for $\varphi = 270^\circ$, where the scalar product $(\mathbf{m} \cdot \mathbf{n})$ is negative and thus $\rho_{\text{trans}}$ has its minimum. In Fig. 3.7(c) for $\mu_0 H = 20\, \text{mT}$ a very small hysteresis and thus a formation of domains, as seen in $\rho_{\text{long}}$ (Fig. 3.7(c)), can be observed, too, but only if the data are plotted on an enlarged scale.

**Oopt configuration**  We finally address the oopt configuration, shown in Fig. (3.9), where the rotation axis is parallel to the in-plane \textbf{t}-vector ($\mathbf{t} = \mathbf{n} \times \mathbf{j}$), leading to $(\mathbf{m} \cdot \mathbf{t}) = 0$. Equations (3.2) and (3.3) then turn to:

\begin{align}
\rho_{\text{long}} &= \rho_0 + \rho_1 (\mathbf{m} \cdot \mathbf{j})^2 + \rho_2 (\mathbf{m} \cdot \mathbf{n})^2 \\
\rho_{\text{trans}} &= \rho_6 (\mathbf{m} \cdot \mathbf{n})
\end{align}
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Figure 3.9: Simulation (lines) and data (open squares) of the 100 nm thick Co$_2$FeAl sample CFA9 at 10 K: (a) $\rho_{\text{long}}$ and (b) $\rho_{\text{trans}}$ in oopt configuration for $\mu_0 H = 20 \text{ mT}$ (black) and $\mu_0 H = 2000 \text{ mT}$ (red).

For $\mu_0 H = 20 \text{ mT}$ in Fig. 3.9(a) a small hysteresis around $\varphi = 0^\circ$ and $\varphi = 180^\circ$ can be observed, more clearly visible at $\varphi = 90^\circ$ and $\varphi = 270^\circ$ in the oopj configuration in Fig. 3.7(c). In contrast to Fig. 3.7, however, the same applied values for the offsets $\rho_0(H)$ do not fit the measured data in the oopt configuration very well.

The reason for this behavior could be the different contacts used for our oopt measurements due to broken wires in the 24-pin Fischer connector cable (between the dipstick and our junction box to which the nanovoltmeters are connected). So instead of using contact 2 and 4 for measuring the longitudinal voltage as before, we had to use contacts 6 and 8 (cf. Fig. 3.6(a) for the positions of the contact pads). Therefore this could lead to a different length $l$ (length difference between the the contact pads in respect to the Hall-bar) in equation (3.1), causing a little change in $\rho_{\text{long}}$. Since $\rho_0 \gg \rho_1$ and $\rho_0 \gg \rho_2$ this change mainly affects $\rho_0$ as can be seen in Fig. 3.9(a).

Comparing $\rho_{\text{trans}}(\varphi)$ in oopt configuration (Fig. 3.9(b)) with the oopj configuration in Fig. 3.7(d) it is evident that the curves have the same shape for $\mu_0 H = 20 \text{ mT}$ and $\mu_0 H = 2000 \text{ mT}$. This is not surprising since Eqs. (3.8) and (3.10) are exactly the same. Thus in both rotation configurations the maximum of $\rho_{\text{trans}}(\varphi)$ for $\mu_0 H = 2000 \text{ mT}$ can
be found in [001] direction. With respect to the hysteresis and generation of magnetic domains for \( \mu_0 H = 20 \text{ mT} \), exactly the same statement as for the oopj configuration holds.

### 3.4.2 ADMR of the 100 nm Thick Co\(_2\)FeAl Sample as a Function of Temperature

In the previous section all three ADMR measurement geometries were discussed in detail for the 100 nm thick Co\(_2\)FeAl film. We now discuss the effect of temperature on the ADMR of this film for \( ip \) configuration. In Fig.3.10 we exemplarily show \( \rho_{\text{long}} \) in \( ip \) configuration, for each temperature normalized to the maximum \( \rho_{\text{long}} \) value so that the data can be compared. \( \rho_{\text{long}}(\varphi) \) is depicted for temperatures of \( T = 10 \text{ K}, 50 \text{ K}, 100 \text{ K}, 150 \text{ K}, 200 \text{ K}, 250 \text{ K}, 300 \text{ K} \) and \( 350 \text{ K} \). For clarity, the simulation was not included in Fig.3.10. With decreasing temperature, the difference between the maximum value and minimum value for the normalized \( \rho_{\text{long}} \), \( \Delta \rho = \frac{\rho_{\text{long, max}} - \rho_{\text{long, min}}}{\rho_{\text{long, max}}} \) is increasing. In Eq. (3.5) this behavior corresponds to an increasing absolute value of \( \rho_1 \) (cf. Tab. 3.2). Reasons for this behavior are discussed later in section 3.4.4.

In Fig.3.11 ADMR measurements of \( \rho_{\text{trans}} \) at fixed temperatures are shown: \( \rho_{\text{trans}}(\varphi) \) at \( 10 \text{ K} \) in panel (a) and at \( 350 \text{ K} \) in (b). In the eight smaller panels (c) - (j) \( \rho_{\text{trans}}(\varphi) \) is depicted at \( T = 10 \text{ K}, 50 \text{ K}, \ldots, 350 \text{ K} \), increasing alphabetically in temperature. In contrast to \( \rho_{\text{long}} \) (Fig.3.10) the \( \rho_{\text{trans}} \) curves qualitatively change as a function of temperature. Between \( T = 100 \text{ K} \) and \( T = 150 \text{ K} \) this change appears, indicated by a shift of the maxima from \( \varphi \approx 135^\circ + n \cdot 180^\circ \) to \( \varphi \approx 45^\circ + n \cdot 180^\circ \) and the minima respectively from \( \varphi \approx 45^\circ + n \cdot 180^\circ \) to \( \varphi \approx 135^\circ + n \cdot 180^\circ \). In Eq. (3.5) this change manifests itself in a change of the sign of parameter \( \rho_7 \) - the planar Hall-effect contribution. The reason for the sign change of \( \rho_7 \) is discussed in detail in section 3.4.4.

### 3.4.3 AMDR Measurement Comparison between the four Co\(_2\)FeAl Samples with Different Thicknesses

After analyzing one Co\(_2\)FeAl thin film for different temperatures, magnetic fields and in different measurement geometries (\( ip, oopj, oopt \)), we now compare films of different thicknesses (20 nm, 50 nm, 80 nm and 100 nm). In Fig.3.12(a) the longitudinal and Fig.3.12(b) the transverse resistivity are depicted for these four films at \( T = 10 \text{ K} \) and a magnetic field of \( \mu_0 H = 20 \text{ mT} \). The resistivities were normalized to the maximum value for each film and plotted versus the rotation angle \( \varphi \). Figure 3.12(a) shows that \( \rho_{\text{long}} \) is only to a
Figure 3.10: Evolution of the longitudinal resistivity $\rho_{\text{long}}(\varphi)$ in $ip$ configuration for the 100 nm thick Co$_2$FeAl sample CFA9, recorded at $\mu_0 H = 20$ mT at the temperatures quoted. For each temperature $\rho_{\text{long}}$ was normalized to its maximum value.
Figure 3.11: ADMR measurements (open squares) and simulation (lines) of the transverse resistivity $\rho_{\text{trans}}(\varphi)$ for the 100 nm thick Co$_2$FeAl film CFA9 in $ip$ configuration, (a) for our lowest temperature ($T = 10$ K) (b) for our highest temperature ($T = 350$ K); the eight smaller graphs (c) - (j) show the ADMR measurements taken at different, fixed temperatures indicated in the graphs, increasing alphabetically in temperature.
very small extent affected by film thickness, since all curves are almost identical in shape.

**Figure 3.12:** ADMR measurements (open squares) and simulation (lines) for (a) the longitudinal resistivity \( \rho_{\text{long}}(\varphi) \) and (b) transverse resistivity \( \rho_{\text{trans}}(\varphi) \) for four Co\(_2\)FeAl samples with different thicknesses (d = 20 nm, 50 nm, 80 nm and 100 nm). The measurements were performed at a temperature of 10 K and a magnetic field of \( \mu_0 H = 20 \text{ mT} \) in \( ip \) rotation configuration. For each film the data were normalized to the maximum value.

In contrast to the longitudinal resistivity the transverse resistivity shows tremendous changes as a function of thickness. Only the two thicker (80 nm and 100 nm) films display the usual behavior as discussed in Sect. 3.4.1, whereas the maxima of the two thinner films (20 nm and 50 nm) are 90°-shifted compared to the maxima of the two thicker (80 nm and 100 nm) films. The sign change of the planar Hall-effect parameter \( \rho_7 \) (cf. Eq. 3.6) describes this behavior and is discussed in the next section.

**3.4.4 Discussion of the Resistivity Parameters**

After having discussed in detail the ADMR measurements and simulation of the four Co\(_2\)FeAl films for different temperatures, magnetic fields, and thicknesses, the essence extracted from the simulation, the resistivity and anisotropy parameters, is analyzed. The first parameter \( \rho_0 \) is independent of the orientation of the magnetization, but depends on the value of the external magnetic field \( \textbf{H} \). It is the only resistivity parameter which
needs to be \( \mathbf{H} \) dependent to get satisfying fitting results. In Fig. 3.13 the resistivity parameters are summarized as a function of \( T \). Exemplarily \( \rho_0 \) is shown here for a field of \( \mu_0 H = 20 \text{ mT} \) (see Fig. 3.13), whereas for other fields the same features are observable. For all samples \( \rho_0 \) is increasing with increasing temperature in quite linear fashion and for low temperatures a saturation of \( \rho_0 \) becomes visible. The behavior for all four films is identical apart from a different offset.

In general, the temperature dependence of the resistivity can be written as \( \rho_{\text{long}}(T) = \rho_{\text{long}}(4 \text{ K}) + cT^m \), where \( m \) is an exponent factor [4]. In a conventional ferromagnetic metal, since one-magnon\(^2\) scattering (or electron-electron scattering) dominates the resistivity at low temperature, \( m \) becomes 2 from theory [47]. For the Heusler compounds, due to the 100\% spin polarization, the one-magnon scattering is suppressed by the factor of \( \exp\left(\frac{d}{k_B T}\right) \) (\( d \) is the energy bandgap for the minority spins at \( E_F \) and \( k_B \) is Boltzmann constant), leading to typically \( m \approx 1.5 \) at low temperature [47]. Epitaxial \( \text{Co}_2\text{FeAl} \) films show \( m = 2.6 \) below 50 K but 1.3 above 100 K [48].

Since \( \rho_0 \gg \rho_1 \) and \( \rho_0 \gg \rho_2 \), the longitudinal resistivity \( \rho_{\text{long}} \) can be approximated by \( \rho_0 \). By fitting our curves with \( \rho_{\text{long}}(T) \approx \rho_0(T) = \rho_0(10 \text{ K}, \text{ 20 mT}) + cT^m \) (cf. Fig. 3.14) for the whole temperature region (\( T = 10 \text{ K} \) to \( T = 350 \text{ K} \)), we get \( m \approx 1.4 \), which corresponds very well to the reported value of \( m = 1.3 \) for \( T > 100 \text{ K} \) [48].

The parameter \( \rho_1 \), which describes the anisotropic magnetoresistance (AMR), is also increasing linearly with rising temperature, but negative for all measured temperatures. The out-of-plane AMR is described by parameter \( \rho_2 \) and is also negative at all temperatures. The behavior of \( \rho_2 \) is totally different for the four films (see Fig. 3.13) and a trend is not visible. Parameter \( \rho_1 \) is twice as large as \( \rho_2 \) and thus has a larger impact on the longitudinal resistivity (cf. Eq. (3.2)).

For the transverse resistivity parameter \( \rho_6 \), which describes the anomalous Hall-effect (AHE), the dominating part is one order of magnitude larger than the planar Hall-effect (PHE) contribution \( \rho_7 \). The AHE is positive for all films and increases linearly with increasing temperature. Using the approximation \( \rho_{\text{long}}(T) \approx \rho_0(T) \) yields the linear proportionality \( \rho_6 \propto \rho_{\text{long}} \), which is an indication that the dominating scattering process causing the AHE is skew scattering [25] (see Sect. 2.2.2.1).

\(^2\)A magnon is a collective excitation of the electrons’ spin structure in a crystal lattice
The PHE parameter $\rho_7$ is different from the others due to its sign change in the two thicker films ($d = 80\,\text{nm}$ and $100\,\text{nm}$). This change appears between $T = 60\,\text{K}$ and $T = 140\,\text{K}$ in these two films. The sign change could be due to a structural change in the thicker films, but then the question arises why we do not see any effect of this structural change in the other resistivity parameters. Bowen et al. also found a change of the sign in the AHE in the Heusler compound Fe$_3$Si, but at a far higher temperature of 251 K [49, 50]. They observed that non-stoichiometric samples Fe$_{3+x}$Si$_{1-x}$ do not show this sign change. So the sign change of $\rho_7$ could indicate a good stoichiometry of the sample.

Since our four Co$_2$FeAl films have $B_2$ structure, the Fe and Al atoms are disordered (cf. Chpt. 2.1), so that the positions of the atoms in the unit cells could be different. This makes the comparison of the curves in Fig. 3.13 more difficult.
3.4.5 Discussion of the Anisotropy Parameters

Apart from the resistivity parameters the anisotropy parameters are crucial. For Co$_2$FeAl the magnetic anisotropy parameters have not yet been quantitatively determined to our knowledge. All three anisotropy parameters $B_{\text{cub}}$, $B_{001}$ and $B_{110}$, which were extracted from the simulation of the ADMR data, are shown in Fig. 3.15 plotted versus the temperature. They are explained in section 2.2.1 and appear in Eq. (3.4).

The uniaxial anisotropy field parameter $B_{001}$, which describes the out-of-plane anisotropy, is very large in comparison to $B_{\text{cub}}$ and $B_{110}$ and varies from 825 mT to about 700 mT with increasing temperature. Within the experimental error all four films show identical behavior and are strictly linear. Thus $B_{001}$ seems to be thickness independent for all Co$_2$FeAl films, revealing that the out-of-plane anisotropy $B_{001}$ is a material property of Co$_2$FeAl. Moreover $B_{001}$ consists of two terms, one is the contribution of the shape anisotropy and the other one is the magneto-elastic term. The shape anisotropy can be estimated by calculating $B_{\text{shape}} = \frac{1}{2} \mu_0 M_S$ (cf. Eq. (2.3)). For a reported saturation magnetization of $M_S = 4.8 \mu_B$/f.u. [43] for Co$_2$FeAl, we obtain $B_{\text{shape}} = 614$ mT. Thus the remaining 86...211 mT in $B_{001}$ are caused by epitaxial strain.

We have an additional in-plane anisotropy $B_{110}$ in the direction of the current density $j$, and the easy axes of the cubic anisotropy, which is negative and much smaller than the uniaxial out-of-plane anisotropy field parameter $B_{001}$ (cf. Fig. 3.15). The anisotropy field parameter $B_{110}$ behaves different for all four films, especially at low temperatures $B_{110}$ ranges from $-3.5$ mT to 0 mT. Thus $B_{110}$ is thickness dependent for Co$_2$FeAl. The origin of this uniaxial in-plane anisotropy parameter, which also appears in other Heusler
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compounds [20, 23, 22] and (Ga,Mn)As thin films, which have also tetragonal crystal
symmetry due to strain in the film growth direction (cf. Chpt. 4), is still under discussion
[20, 21, 22, 23]. Suggested reasons are strain [20] or the large lattice mismatch between
substrate and film [22].

Furthermore we have an additional in-plane component, the cubic anisotropy $B_{\text{cub}}$, which
is responsible for the two hard and easy axes in Co$_2$FeAl. The anisotropy field parameter
$B_{\text{cub}}$ shows for all four films an identical behavior, so that this is besides $B_{001}$ the second
anisotropy parameter which is thickness independent. Thus the cubic anisotropy is also
a material property of Co$_2$FeAl. So we have only $B_{110}$ left which shows a dependence on
the thickness of the films. Hence, the growth and annealing process of the films could
influence this parameter.

Figure 3.15: Anisotropy parameters of the investigated Co$_2$FeAl thin films plotted as a function
of temperature, extracted from the simulation of the data.
Comparison of the Magnetic Anisotropy in Different Heusler Compounds  

We now briefly compare our values of the cubic and uniaxial in-plane anisotropy with values of other groups. Since no anisotropy values for Co\textsubscript{2}FeAl could be found in the literature, we have to compare with other Heusler compounds. Yilgin et al. investigated Co\textsubscript{2}MnSi thin films grown on MgO (001) substrates. They found a cubic anisotropy of \(B_{\text{cub}} = -1.2 \ldots 17.5\) mT and a uniaxial anisotropy of \(B_{\text{u}} = 0.5 \ldots 1.2\) mT at room temperature, depending on annealing [51]. Co\textsubscript{2}MnGa films grown on GaAs (001) were investigated by Pechan et al., who discovered a cubic anisotropy of \(B_{\text{cub}} = 0.83 \ldots 1.29\) mT and a uniaxial anisotropy of \(B_{\text{u}} = 0.31 \ldots 1.59\) mT at room temperature, depending on the strain in the sample [20]. Comparing our values (shown in Fig. 3.15) to those of Yilgin et al., we conclude that they have the same order of magnitude, whereas the cubic anisotropy of the Co\textsubscript{2}MnGa thin films is much smaller.

3.5 Conclusion and Future Prospects

In this chapter we reported about the measurement setup, including our self-made sample carrier system for the dipstick which allows us to perform ADMR measurements. The ADMR measurements were performed in a superconducting split coil magnet cryostat investigating four Co\textsubscript{2}FeAl thin films of different thicknesses \((d = 20, 50, 80 \text{ and } 100\) nm\) at temperatures of \(T = 10, 50, 100, 150, 200, 250, 300, 350\) K and at magnetic fields of \(\mu_0H = 20, 40, 200, 500, 1000, 2000\) mT. We presented three measurement geometries, \(ip\), \(oopj\) and \(oopt\). For the simulation of the data the phenomenological resistivity model, discussed in the theory section 2.2.2.3, was applied. It was sufficient to use parameters up to the second order of magnetization for the fitting process to describe all data very well. We exemplarily discussed the 100 nm thick Co\textsubscript{2}FeAl film for all three measurement geometries in detail and explained the shape of the longitudinal \(\rho_{\text{long}}(\varphi)\) and transverse \(\rho_{\text{trans}}(\varphi)\) resistivity curves.

From the simulation of the measured data we extracted the resistivity parameters and magnetic anisotropy parameters. To our knowledge this is the first quantitative determination of the magnetic anisotropy parameters for Co\textsubscript{2}FeAl. We fitted the temperature dependence according to \(\rho_{\text{long}}(T) = \rho_{\text{long}}(4\text{K}) + cT^m\) [4], approximating \(\rho_{\text{long}}\) by \(\rho_0\), and found \(m \approx 1.4\), which is in good agreement with \(m = 1.3\), reported by Kelekar et al. [48] (for Co\textsubscript{2}FeAl thin films for temperatures above 100 K). For the AHE parameter \(\rho_6\) we discovered that skew scattering is the dominating process, since \(\rho_6 \propto \rho_{\text{long}}\). As a crucial
result, we observed a sign change of the PHE parameter \( \rho \) for the 80 nm and 100 nm thick Co\(_2\)FeAl film, which occurs between \( T = 60 \) K and \( T = 140 \) K. One reason could be a structural change in the thicker films. However, the question arises why we did not see any effect of this structural change in the other parameters. Bowen et al. also observed this sign change of the PHE in Heusler Fe\(_{3+x}\)Si\(_{1-x}\) thin films, but only for films with \( x = 0 \), and not for non-stoichiometric samples [49, 50]. Hence, the sign change could be a indicator for good stoichiometry.

The out-of-plane anisotropy parameter \( B_{001} \) is two orders of magnitude larger than the other two anisotropy parameters, \( B_{110} \) and \( B_{cub} \) and consists of two contributions: the shape anisotropy and the magneto-elastic anisotropy. The calculation of the shape anisotropy contribution \( B_{shape} = \frac{1}{2} \mu_0 M_S \) yields that more than 75\% of the out-of-plane anisotropy is caused by the shape of the film. We found that the cubic in-plane anisotropy \( B_{cub} \) and the uniaxial out-of-plane anisotropy \( B_{001} \) are thickness independent leading to the conclusion that both parameters are material properties of Co\(_2\)FeAl. The uniaxial in-plane parameter \( B_{110} \) is not thickness independent and its origin is still under discussion. Suggested reasons causing this uniaxial in-plane anisotropy are strain [20] and a large lattice mismatch between substrate and film [22]. Comparing our anisotropy parameters with those of other Heusler compounds, it turns out that they have the same order of magnitude.

We conclude that the ADMR measurement method and the simulation of the data works very well in Co\(_2\)FeAl. Although we only presented Co\(_2\)FeAl, first ADMR experiments with Co\(_2\)MnSi look promising. For further ADMR studies it would be interesting to see if the sign change of the PHE also exists in other Heusler compounds, like Co\(_2\)MnSi or Co\(_2\)FeSi (Bowen et al. [49, 50] reported about this phenomenon in Fe\(_3\)Si) and if the anisotropy parameters \( B_{001} \) and \( B_{cub} \) are also thickness independent in these materials.
Chapter 4

Caloritronic Experiments

As discussed in chapter 2.3, one important goal of this thesis is to measure the influence of the magnetization orientation on the thermopower. In analogy to ADMR (see chapter 3) these ADMTP measurements can be described with a symmetry-based power series approach. In order to test the caloritronics setup assembled during this thesis, we decided to study the anisotropic thermopower of (Ga,Mn)As thin films first because of its high AMR (see 2.2.2.2), which can be seen in the resistivity anisotropy ratio $\rho_1/\rho_0 \sim 1\ldots3$ in (Ga,Mn)As [35] (Mn concentration: 3%). In contrast, in Heusler compounds we have $\rho_1/\rho_0 \sim 0.08\%$ which leads to a small ADMTP. (Ga,Mn)As is a ferromagnetic semiconductor, obtained by doping GaAs with a small percentage (about 2\ldots6%) of manganese. For the first time this magnetic semiconductor was fabricated and investigated 1996 by Ohno et al. [53]. In a recent review article about (Ga,Mn)As by Gould et al. more detailed information about the material system can be found [54].

This chapter starts with a detailed description of the caloritronic measurement setup. We then take a closer look at the ADMTP data and simulations in (Ga,Mn)As thin films and compare them with literature. We especially discuss the influence of the Seebeck parameter $S_C$ on the simulation of the transverse thermoelectrical voltage. Finally, we report on our ADMTP experiments with Co$_2$FeAl and conclude with a summary and outlook.

4.1 Measurement Setup

Our measurement setup can be seen in Fig. 4.1 where the sample is already fixed on the dipstick head. The (Ga,Mn)As sample was cut into a rectangular bar with a length of

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Figure 4.1: Picture of the caloritronic dipstick head for thermoelectrical measurements with labeled component parts.

Figure 4.2: Sketch of the contacted bar, with negative and positive polarity of the contacts, magnetic field and thermal gradient direction as indicated. $\phi$ is the angle between the magnetic field $H$ and the direction [110]. The abbreviation $\text{therm.}$ stands for thermoelectric.
4 mm and a width of 2 mm and was glued with GE varnish [45] between two copper blocks. The position of the lower block in Fig. 4.1 can be adjusted by a screw so that samples with different lengths up to 5 mm fit into the setup. The lower block is thermally anchored to the dipstick head, whereas the upper block is thermally isolated via a plastic block. On the upper block a resistor and a Pt10k temperature sensor\(^2\) are glued with GE varnish to guarantee good thermal coupling. The resistor on the upper copper block serves as a resistive heater to establish higher temperatures than on the other block, which is at the base temperature of the dipstick. On the lower block a second Pt10k temperature sensor is fixed. The only thermal connection (apart from the He gas atmosphere in the cryostat) between the two blocks is the sample, so that a temperature gradient is generated. On the left and right side of the copper blocks, contact pads are positioned along the sample which connect the heater, temperature sensors and the sample with the other end of the dipstick which is in turn connected to the measurement devices. Six bonds are placed on the sample, two on both ends of the bar to enable measurements of the longitudinal voltage in a four point method (for resistivity characterization) and the other two on both sides in the middle of the bar measuring the transverse voltage (see Fig. 4.2). The dipstick head was designed by D. Venkateshvaran and improved by myself (new resistor and new wire connections).

After mounting the sample on the dipstick head, the dipstick was placed into a superconducting split coil magnet cryostat (Oxford Instruments SM4000) with a maximum magnetic field of \(\pm 7\) T. The field is oriented perpendicular to the dipstick axis, so that the magnetic field always lies in the sample plane. Therefore it is not possible to conduct out-of-plane measurements. The dipstick is located inside the variable temperature insert (VTI) in the cryostat which can be cooled down to 2.4 K. For the temperature control an Oxford ITC 503S (intelligent temperature control) device was used. In the dipstick head an additional heater is placed to adjust the base temperature of the dipstick. As the lower copper block is thermally connected to the dipstick, this defines the temperature at the 'cold' side of the sample. It is controlled by a Lakeshore 340 Temperature Control unit. A second Lakeshore 340 is connected to the resistor and temperature sensor on the 'hot' block. Therefore, a well defined temperature gradient between the hot and the cold block can be established and thus between both ends of the sample. The measured temperature gradient in the sample itself will be somewhat smaller than the temperature difference between the copper blocks. The Pt10k temperature sensors have a detection range from

\(^2\)Pt10k is a platinum sensor which has a resistance of 10 kΩ at 0°C.
73 K up to 873 K. A stepping motor (OWIS DMT 100) is used to rotate the dipstick with respect to \(\textbf{H}\), equivalent to a rotation of the magnetic field \(\textbf{H}\) in relation to \(\nabla T\).

In the setup a 100 \(\Omega\), 1.5 W resistor is used (before it was a 3 \(\Omega\), 3 W resistor) to get a more precise control of the heater output especially at low temperatures. The angle dependent thermopower measurements (ADMTP) and angle dependent magnetoresistance (ADMR) measurements are performed at a constant applied field \(\textbf{H}\) and a constant temperature. During the measurement the magnetic field is rotated from -30° to 380° and back to -30° in 2° steps so that there is a small overlap between forth and back sweep. That way, one can verify if the data at the angle \(\varphi\) and \(\varphi + 360°\) have the same value, i.e., if they are consistent. The longitudinal and transverse voltage at each \(\varphi\) are acquired by Keithley K2182 nanovoltmeters. In the ADMR measurements, instead of a temperature gradient, a current is applied from one end to the other end of the sample by a Keithley K2400 sourcemeter and voltages acquired in a four point measurement. LabVIEW-based software was used to control all the measurement devices and for data acquisition. Before the ADMTP measurement is started a predefined starting position must be established and a high magnetic field (2 – 3 T) must be applied first in order to guarantee the same starting orientation for the magnetization, as we did in the ADMR measurements in chapter 3.

4.2 Anisotropic Magnetothermopower of (Ga,Mn)As Films

Sample Growth We have investigated two (Ga,Mn)As samples, both fabricated at the university of Ulm (group of Avrutin et al.) by molecular beam epitaxy (MBE) [55]. Both samples were grown on (001)-oriented GaAs substrates. The first Ga\(_{1-x}\)Mn\(_x\)As film investigated (sample B374) is 180 nm thick and has a manganese concentration of \(x = 0.03\), the second one (B636) is only 30 nm thick, with \(x = 0.045\).

Measurements and simulation Before discussing thermopower results, we first want to show that the thermoelectric voltages observed are proportional to the heater power output and therefore to the thermal gradient. Figure 4.3 shows data from sample B374, recorded at a dipstick temperature \(T_{\text{dipstick}} = 10\,\text{K}\). This is the lowest temperature at which we have been able to achieve a stable temperature difference between the hot and cold end of the sample. In our measurements the temperature gradient \(\nabla T\) is always
applied in the [110] direction along the film bar as indicated in Fig. 4.2. Figure 4.3 indicates that the longitudinal thermoelectric voltage scales linearly with the heater power. The linear fit goes through the origin (apart from a very small offset which probably is caused by small temperature fluctuations we had during this measurement). A slightly bended fit curve would also describe the data very well. Reasons for this small deviation from the linear behavior could be an unwanted heat dissipation via the bond wires or the surrounding He-gas. Nevertheless there is indication that the thermoelectric voltage is linearly proportional to the heating power which implies $V \sim \Delta T$. As the Pt10k thermometers are not reliable at $T_{\text{dipstick}} = 10$ K it was not possible to quantify $\Delta T$. Figure 4.3 shows that it is sufficient to record $V_{\text{long}} \propto \alpha_{\text{long}} = -\frac{V_{\text{long}}}{\Delta T}$ as a measure of the thermopower.

![Graph](image)

Figure 4.3: Longitudinal thermoelectric voltage of the (Ga,Mn)As thin film B374 at 10 K plotted versus the heater power (black dots). The red line is a linear fit to the measured data points with the given values for intercept and slope as indicated.

We now present the caloritronic measurements performed on the two (Ga,Mn)As films at $T_{\text{dipstick}} = 10$ K. In Fig. 4.4 the ADMR and ADMTP measurements of the 180 nm thick Ga$_{0.97}$Mn$_{0.03}$As film B374 are plotted together with the corresponding simulations. In all four panels $\rho(\varphi)$ or $V_{\text{therm.}}(\varphi)$ are plotted versus the angle $\varphi$ for $\mu_0 H = 50$ mT (black color) and $\mu_0 H = 1000$ mT (red color) in $ip$ geometry (see Fig. 2.5). $\varphi$ is the angle between the magnetic field $\mathbf{H}$ and the [1$\bar{1}$0] direction ($\varphi = \angle(\mathbf{H},[1\bar{1}0])$). The temperature gradient was applied along the [110] direction, parallel to the long side of the (Ga,Mn)As bar, as indicated in Fig. 4.2. The resistive heater output was constantly $P_{\text{heater}} = 0.48$ W. The (Ga,Mn)As samples have a tetragonal crystal symmetry instead of a cubic due to the shape of the film and the strain in the [001] growth direction. For
the fitting procedure in (Ga,Mn)As we could not achieve good results when we only used
the first and second order terms in the resistivity tensor and respectively in the Seebeck
tensor. Thus we included the third and fourth order terms in our fit equations (compare
the original Eq. (2.26), (2.27), (2.35) and (2.36)):

\[
\rho_{\text{long}} = \rho_0 + \rho_1 (j \cdot m)^2 + \rho_3 (j \cdot m)^4 \\
\rho_{\text{trans}} = \rho_7 (j \cdot m)(t \cdot m) \\
\alpha_{\text{long}} = S_0 + S_1 (j \cdot m)^2 + S_3 (j \cdot m)^4 \\
\alpha_{\text{trans}} = S_7 (j \cdot m)(t \cdot m) + S_C (j \cdot m)^3(t \cdot m)
\]

(4.1) (4.2) (4.3) (4.4)

So, after a comparison of the Eq. (4.1), (4.2), (4.3) and (4.4), we observe that only in
the transverse thermopower \( \alpha_{\text{trans}} \), Eq. (4.4), a new coefficient \( S_C \) appears; otherwise the
equations are the same. In the following, we use thermopower and thermoelectric voltage
as equivalent terms, because they are proportional to each other.

4.2.1 Discussion of the Experimental Data and Simulation

When we compare the longitudinal part of the resistivity in Fig. 4.4(a) with the ther-
omelectric voltage in Fig. 4.4(c), we see that \( \rho(\varphi) \) has a clearly different magnitude for
\( \mu_0 H = 1000 \text{ mT} \) and \( 50 \text{ mT} \), while the magnitude of \( \alpha(\varphi) \) is essentially independent of
\( |H| \). This is also evident from Tab. 4.1, in which all resistivity and anisotropy parameters
are summarized. The dependence of \( \rho_0(H) \) on \( H \) is analogous to the \( \rho_0(H) \) observed in
the ADMR measurements in Heusler compounds (compare Chpt. 3.4.1). \( \rho_0(H) \) is found
to decrease with increasing magnetic field, reflecting the negative magnetoresistance be-

\[ \rho_0(50 \text{ mT}) = -126 \mu\text{V} \] in comparison
to \( S_0(1000 \text{ mT}) = -126.7 \mu\text{V} \). This contradicts the assumption by Pu et al. that \( \alpha_{\text{long}} \)
saturates at magnetic fields of \( \sim 200 \text{ mT} \). To confirm this fact we also performed
AMR measurements up to \( 7 \text{ T} \) and found that the longitudinal thermopower is linearly
decreasing with increasing field \( H \) (see Fig. 4.5). We performed these measurements at
10 K for both (Ga,Mn)As samples at different field orientations (\( \varphi = 0^\circ \) shown in Fig. 4.5)
and got always the same results for \( V_{\text{therm., long}} \): a linearly decreasing dependence on \( \mu_0 H \).
Note that both curves were symmetrized to get rid of transverse contributions in the
longitudinal thermoelectrical voltages.
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Anisotropic Magnetothermopower of (Ga,Mn)As Films

Figure 4.4: (a) longitudinal resistivity (b) transverse resistivity (c) longitudinal thermoelectric voltage (d) transverse thermoelectric voltage - plotted versus the orientation $\varphi$ of the external magnetic field $\mathbf{H}$ in the 180 nm thick Ga$_{0.97}$Mn$_{0.03}$As film B374 for $T_{\text{dipstick}} = 10$ K and $P_{\text{Heater}} = 0.48$ W. Open squares represent experimental data, the lines are simulations according to Eqs. (4.1)-(4.2).
Another fact is that the Seebeck coefficient \( \alpha \propto -V_{\text{therm}} \) is positive, showing that charge transport is via holes, as already reported by Pu \textit{et al.}, Osinniy and Mayer \cite{56,57,58}. The maxima in Fig. 4.4(a) and (c) are at \( 0^\circ + n\cdot180^\circ \) whereas the minima are at \( 90^\circ + n\cdot180^\circ \), which is also the case for the Heusler alloys (cf. 3.4.1). The reason for the same position of the minima/maxima is the tetragonal crystal structure.

The transverse resistivity (Fig. 4.4(b)) and transverse thermoelectric voltage (Fig. 4.4(d)) have the typical shapes discussed in the context of the ADMR measurements (see Chpt. 3.4.1). As \( \rho_{\text{trans}} \) and \( V_{\text{therm, trans}} \) have quite similar shape, the additional parameter \( S_C \) in the transverse Seebeck coefficient must be small in comparison to the \( S_7 \) (Nernst effect) parameter. Indeed, \( S_C \) is about one order of magnitude smaller than \( S_7 \) as can be seen in Tab. 4.1. A detailed discussion whether or not this parameter is needed to describe our data is presented later.

![Figure 4.5: Anisotropic magnetoresistance (AMR) measurement of both (Ga,Mn)As samples at a temperature of 10 K and with the magnetic field \( H \) oriented perpendicular to the thermal gradient (\( \varphi = 0^\circ \)). Both curves were symmetrized to get rid of transverse contributions in the longitudinal thermoelectrical voltages.](image)

**4.2.1.1 Shifted Easy and Hard Axis**

The hard axis of the magnetic anisotropy can clearly be identified in both panels lying about \( 7^\circ \) shifted from the \([110]\) and \([110]\) directions. To explain this behavior we take a look at the free energy surface for both (Ga,Mn)As films (compare Chpt. 2.2.1)

\[
F_{\text{tot,M}} = B_{100}m_x^2 + B_{\text{cub}}(m_x^4 + m_y^4 + m_z^4) + \frac{1}{2}B_{110}(m_x - m_y)^2
\]  

(4.5)

where we only take \textit{in-plane} magnetic anisotropies into account and have set the Zeeman
term to zero. We want to study the free energy surface when the magnetization rotates in-plane: \( m_x = \cos(\varphi) \), \( m_y = \sin(\varphi) \) and \( m_z = 0 \). We plug in the anisotropy values from Tab. 4.1 acquired by our simulation. Figure 4.6 shows the free energy surface (blue) whose maxima and minima define the hard (green) and easy axis (orange). As we can undoubtedly see these shifts out of the [1\textbar10] and [110] directions are already visible in the free energy surface and are caused by the uniaxial anisotropy parameter \( B_{\text{1\textbar10}} \) according to Pappert et al. [59].

![Figure 4.6: In-plane free energy (blue) surface plotted versus the rotation angle \( \varphi \) for (a) Ga\textsubscript{0.97}Mn\textsubscript{0.03}As (B374) and (b) Ga\textsubscript{0.955}Mn\textsubscript{0.045}As (B636). The maxima and minima of the free energy surface determine the hard (green) and easy axis (orange), which are slightly shifted out of their tetragonal symmetry positions. As a comparison the transverse resistivity data, measured at 10 K and 50 mT (black open squares), and simulation (black line) is shown.](image)

### 4.2.1.2 Relative Magnetothermopower

We now compare the relative longitudinal and transverse magnetothermopower \( \frac{\Delta \alpha}{\alpha} = \left| \frac{\Delta V_{\text{therm.}}}{V_{\text{therm.}}} \right| = \left| \frac{V_{\text{therm.}}(\text{max}) - V_{\text{therm.}}(\text{min})}{V_{\text{therm.}}(\text{max})} \right| \) in our measurements with those of Pu et al. who investigated amongst others a 3.9\% doped (Ga,Mn)As thin film at a temperature of 6 K [56]. They used a step-heating method to measure the thermal voltage change \( \Delta V \) and could therefore directly calculate the Seebeck coefficient. We calculated \( \frac{\Delta \alpha}{\alpha} \bigg|_{\text{long}} = \left| \frac{V_{\text{therm.\ long}}(\text{max}) - V_{\text{therm.\ long}}(\text{min})}{V_{\text{therm.\ long}}(\text{max})} \right| \) for both (Ga,Mn)As films at 10 K and 1000 mT,
where \( \mathbf{M} \) should be fully aligned with \( \mathbf{H} \), and got \( \left. \frac{\Delta \alpha}{\alpha} \right|_{\text{long}} \approx 7.2\% \) for \( \text{Ga}_{0.97}\text{Mn}_{0.03}\text{As} \) and \( \left. \frac{\Delta \alpha}{\alpha} \right|_{\text{long}} \approx 4.8\% \) for \( \text{Ga}_{0.955}\text{Mn}_{0.045}\text{As} \). Pu et al. calculated \( \left. \frac{\Delta \alpha}{\alpha} \right|_{\text{long}} \approx 6.3\% \) (for \( \mu_0H = 200\text{ mT} \)) which lies between our two calculated values. Taking into account that the manganese percentage of their film is also in between ours, the values are in good agreement with each other, although we measured at a 4 K higher temperature. For the relative transverse magnetothermopower \( \frac{\Delta \alpha}{\alpha} \big|_{\text{trans}} \approx \frac{\left| V_{\text{therm., trans}}^{(\text{max})} - V_{\text{therm., trans}}^{(\text{min})} \right|}{V_{\text{therm., long}}^{(\text{max})}} \) we get \( \left. \frac{\Delta \alpha}{\alpha} \right|_{\text{trans}} \approx 1.1\% \) for \( \text{Ga}_{0.97}\text{Mn}_{0.03}\text{As} \) and \( \left. \frac{\Delta \alpha}{\alpha} \right|_{\text{trans}} \approx 1.0\% \) for \( \text{Ga}_{0.955}\text{Mn}_{0.045}\text{As} \), whereas Pu et al. calculate \( \left. \frac{\Delta \alpha}{\alpha} \right|_{\text{trans}} \approx 4.2\% \). As we can see, our calculated values for relative transverse magnetothermopower in both samples are about 3\% smaller. A possible reason could be the higher temperature at which we measured.

We can also confirm that \( \alpha_\parallel > \alpha_\perp \) where \( \alpha_\parallel \) (\( \alpha_\perp \)) is the longitudinal thermopower when \( \mathbf{M} \) is parallel to \( \nabla T \), \( \varphi = 90^\circ \) (perpendicular; \( \varphi = 0^\circ \)) and \( \rho_\parallel < \rho_\perp \) which is typical for GaMnAs [56, 54].

### 4.2.1.3 Asymmetry

Another eye-catching point is the asymmetric behavior of the ADMTP curves, especially visible in Fig. 4.4(c). A possible reason for this could be a non-zero out-of-plane contribution due to a little tilt misalignment of the sample as discussed before in the ADMR section (3.4.1). Another possibility could be the inhomogeneous Helium gas flow in the cryostat, which could cause small temperature fluctuations in the gas around the sample, although the dipstick head is capped. In the film bar the temperature gradient is supposed to be homogeneous along the bar, but this is probably not the case due to a heat dissipation via the bond wires.

Apart from this asymmetry the shape of the curves in Fig. 4.4(a) and (c) are very similar due to the same fitting equations. Nevertheless the simulation fits the measured data for both thermopower and resistivity reasonably well.

Figure 4.7 shows the same compilation of experimental and simulation data as in Fig 4.4, this time for the 30 nm thick \( \text{Ga}_{0.955}\text{Mn}_{0.045}\text{As} \) film B636. If we take a closer look at the panels we observe that the simulation fits the experimental data better due to a smaller asymmetry behavior, which was discussed above for the B374 sample. In comparison to the thicker and less doped sample the resistivity of B636 is about a two-thirds larger. The higher doping concentration leads to a larger scattering rate with the dopant and thus to

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\(^3\)Note that we use the longitudinal voltage as normalization factor.
Figure 4.7: (a) longitudinal resistivity (b) transverse resistivity (c) longitudinal thermoelectric voltage (d) transverse thermoelectric voltage - plotted versus the orientation $\phi$ of the external magnetic field $\mathbf{H}$ in the 30 nm thick Ga$_{0.955}$Mn$_{0.045}$As film B636 for $T_{\text{dipstick}} = 10$ K and $P_{\text{Heater}} = 0.48$ W. Open squares represent experimental data, the lines are simulations according to Eqs. (4.1)-(4.2).
a larger resistivity. Impurity scattering plays the dominant role at 10 K. We now compare
the longitudinal resistivity from our measurements with M. Althammer’s measurements
on the B636 sample [19]. He got a maximum resistivity of 108.2 \( \mu \Omega \text{m} \) at \( T = 10 \text{ K} \) and
\( \mu_0 H = 1000 \text{ mT} \) whereas we get a \( \sim 25 \% \) higher resistivity of 138.5 \( \mu \Omega \text{m} \). One reason for
this deviation could be the when calculating the resistivity with Eq. (3.1), the length and
width goes into the formula, both afflicted with some uncertainty of about 200 \( \mu \text{m} \). If the
bonds are not exactly at the edges of the film this could also affect the resistivity.

Another observation is that the longitudinal thermopower \( \alpha_{\text{long}} \propto -V_{\text{therm., long}} \) is larger in
the B636 sample whereas the transverse thermopower is smaller than in the B374 sample.
To explain this observation a more detailed analysis of a series of (Ga,Mn)As films with
different fabrication parameters is needed and we have to redesign our measurements setup
so that we can quantitatively measure the thermopower, not only qualitatively. Never-
theless, ADMTP measurements could be successfully established in this thesis. Detailed
studies will follow in the future.

Fitting Parameter Comparison In Tabs. 4.1 and 4.2 a comparison of the anisotropy,
resistivity and Seebeck coefficient fitting parameters of B374 and B636 are given. We
used the same anisotropy parameters for the resistivity and thermopower and could fit
the measured data quite well. Only \( \rho_0 \) and \( S_0 \) are \( H \)-field dependent, but the changes in
\( S_0 \) are so small that the parameter could also be set constant and thus field independent.

4.2.2 Anisotropy Parameter Discussion

We see that the anisotropy parameters are nearly the same for both films apart from the
\( B_{110} \) parameter which has a different sign. The origin of this uniaxial \( \text{in-plane} \) anisotropy
parameter is still under discussion [21, 60, 61], but the parameter, and especially its sign,
can be influenced by annealing [21], varying the hole concentration \( p \) [60] and also tem-
perature [21]. Welp et al. [61] discovered that this anisotropy parameter is thickness
independent. In the studies for Co\(_2\)FeAl we observed a thickness dependence of the cor-
responding \( B_{110} \) parameter (see Sect. 3.4.5). In the ADMR measurements of the Heusler
films we did not need a \( B_{100} \) parameter; but this parameter has to be included here in
order to obtain a good fit. Gould and Pappert et al. observed in their anisotropy inves-
tigations in (Ga,Mn)As two uniaxial \( \text{in-plane} \) anisotropies in [100] and [\( \bar{1}10 \)] directions in
addition to the cubic anisotropy [59, 54, 62]. They used the so called ‘anisotropy finger-
print’ technique which is based on the angular dependence of the magnetization switching
fields. They summarized all their transport measurements into color coded resistance polar plots (RPPs) which act as fingerprints for the anisotropy of a given structure. This technique is in detail discussed by Pappert et al. [59]. The origin of this additional anisotropy which points in the direction of the easy or hard axis of the cubic anisotropy, depending on the doping concentration, is still under discussion. It is assumed to result from some extrinsic symmetry breaking introduced during growth and/or processing of the layers. However, attempts to relate it to specific parameters, such as substrate miss-cut, surface reconstruction, and strain, have proven inconclusive so far [54]. As a rough rule of thumb, the relative strength of these anisotropy terms is of the order of $B_{cub} : B_{110} : B_{010} \sim 25 : 10 : 1$ at 4 K [59]. For higher temperatures up to the Curie temperature $T_C$ the uniaxial parameters become larger whereas the cubic anisotropy decreases. Regarding our anisotropy parameters in respect to the rule of thumbs the $B_{100}$ anisotropy is much larger. The reason is probably the temperature dependence.

### 4.2.3 Discussion of the Seebeck Coefficient $S_C$

The higher order terms $S_3$ and $S_C$ for the Seebeck coefficient are about one order in magnitude smaller than the $S_1$ and $S_7$ parameters, so that the effect of the $S_C(V)$ parameter is very small, in agreement with the expectations we made in the theory chapter 2.3.2. We now discuss whether the $S_C$ parameter is necessary for the fitting procedure. Therefore we do two fits for both (Ga,Mn)As samples as can be seen in Fig. 4.8, one time with the $S_C$ term (depicted in green) and one time without (blue) it. In Fig. 4.8(a) and (c) we see the plot for the Ga$_{0.97}$Mn$_{0.03}$As film B374 and in Fig. 4.8(b) and (d) for the Ga$_{0.955}$Mn$_{0.045}$As film B636. In the linear plots the difference between the curves can be seen more easily. The influence of the parameter $S_C$ is very small, but it can be definitely observed that the green curves fit the data slightly better, especially for the B374 sample in Fig. 4.8(c). The $S_C$ parameter is responsible for a small tilt of the curve in the linear plots. In Tab. 4.3 the new values for $S_7$ can be seen which differ from the values in Tab. 4.2 when $S_C$ is non-zero. It is still arguable if the $S_C$ is really needed; for the $ip$ measurements of both (Ga,Mn)As samples the parameter is not absolutely necessary and the theory of the Seebeck coefficients does not need to be applied to get reasonable fitting results. Only out-of-plane measurements, where the influence of the $S_A$ and $S_B$ parameters might be seen, will be able to reveal whether the new phenomenological Seebeck tensor theory is needed or not.
Figure 4.8: Comparison of the influence of parameter $S_C$ on the fit. In the green curve the fit was done with $S_C$ whereas in the blue curve the fit was done without the $S_C$ term. In panel (a) and (c) the Ga$_{0.97}$Mn$_{0.03}$As film B374 is plotted in a polar and in (c) in a linear plot respectively. The same was done with the Ga$_{0.955}$Mn$_{0.045}$As film B636 in panel (b) and (d); $T_{\text{dipstick}} = 10$ K and $\mu_0 H = 50$ mT. Open squares represent experimental data, the lines are simulations according to Eqs. (4.1)-(4.2).
Table 4.1: Resistivity and anisotropy simulation parameters for fitting the resistivity in the (Ga,Mn)As samples B374 and B636

<table>
<thead>
<tr>
<th>GaMnAs</th>
<th>$\rho$ (B374)</th>
<th>$\rho$ (B636)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{001}$ (T)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>$B_{cub}$ (T)</td>
<td>-0.013</td>
<td>-0.009</td>
</tr>
<tr>
<td>$B_{100}$ (T)</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>$B_{1\bar{1}0}$ (T)</td>
<td>-0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>$\rho_0(50 \text{ mT})(\text{n}\Omega\text{m})$</td>
<td>8.6085</td>
<td>13.847</td>
</tr>
<tr>
<td>$\rho_0(100 \text{ mT})(\text{n}\Omega\text{m})$</td>
<td>8.5959</td>
<td>13.816</td>
</tr>
<tr>
<td>$\rho_0(500 \text{ mT})(\text{n}\Omega\text{m})$</td>
<td>8.5590</td>
<td>13.628</td>
</tr>
<tr>
<td>$\rho_0(1000 \text{ mT})(\text{n}\Omega\text{m})$</td>
<td>8.4105</td>
<td>13.440</td>
</tr>
<tr>
<td>$\rho_1(\text{n}\Omega\text{m})$</td>
<td>-0.054</td>
<td>-0.0387</td>
</tr>
<tr>
<td>$\rho_3(\text{n}\Omega\text{m})$</td>
<td>-0.108</td>
<td>-0.0933</td>
</tr>
<tr>
<td>$\rho_7(\text{n}\Omega\text{m})$</td>
<td>-0.2196</td>
<td>-0.243</td>
</tr>
</tbody>
</table>

Table 4.2: Seebeck coefficient and anisotropy simulation parameters for fitting the thermopower in the (Ga,Mn)As samples B374 and B636

<table>
<thead>
<tr>
<th>GaMnAs</th>
<th>$\alpha_{\text{therm.}}$ (B374)</th>
<th>$\alpha_{\text{therm.}}$ (B636)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{001}$ (T)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>$B_{cub}$ (T)</td>
<td>-0.013</td>
<td>-0.009</td>
</tr>
<tr>
<td>$B_{100}$ (T)</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>$B_{1\bar{1}0}$ (T)</td>
<td>-0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>$S_0(50 \text{ mT})(\text{µV})$</td>
<td>-126</td>
<td>-148.8</td>
</tr>
<tr>
<td>$S_0(100 \text{ mT})(\text{µV})$</td>
<td>-126.2</td>
<td>-148.8</td>
</tr>
<tr>
<td>$S_0(500 \text{ mT})(\text{µV})$</td>
<td>-125.7</td>
<td>-149.1</td>
</tr>
<tr>
<td>$S_0(1000 \text{ mT})(\text{µV})$</td>
<td>-126.7</td>
<td>-149.9</td>
</tr>
<tr>
<td>$S_1(\text{µV})$</td>
<td>-8</td>
<td>-5.8</td>
</tr>
<tr>
<td>$S_3(\text{µV})$</td>
<td>-0.6</td>
<td>-0.5</td>
</tr>
<tr>
<td>$S_7(\text{µV})$</td>
<td>-2.3</td>
<td>-1.39</td>
</tr>
<tr>
<td>$S_C(\text{µV})$</td>
<td>-0.6</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

Table 4.3: Seebeck coefficient $S_7$ when fitting is done without the $S_C$ parameter in the (Ga,Mn)As samples B374 and B636

<table>
<thead>
<tr>
<th>GaMnAs</th>
<th>$\alpha_{\text{therm.}}$ (B374)</th>
<th>$\alpha_{\text{therm.}}$ (B636)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_7(\text{µV})$</td>
<td>-2.55</td>
<td>-1.28</td>
</tr>
<tr>
<td>$S_C(\text{µV})$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
4.3 Experiment and Simulation in Co$_2$FeAl Films

We also attempted to perform ADMTP measurements on the Co$_2$FeAl Heusler thin films, in which we already successfully conducted ADMR measurements. We used the same measurement setup as for the (Ga,Mn)As samples. A 80 nm thick Co$_2$FeAl film was cut into a bar, positioned between the copper blocks and contacted in the same fashion as we did with the (Ga,Mn)As samples. We detected a thermoelectrical voltage signal of $\sim 95$ $\mu$V and therefore a negative thermopower $\alpha < 0$, as expected for Heusler thin films. However, in the ADMTP measurements the $M$-orientation-dependent change in thermoelectric voltage is $\Delta V \propto -\Delta \alpha / \alpha < 0.3\%$ and thus too small to be resolved with the current setup (see Fig. 4.9). But this was to be expected because $\Delta \rho / \rho$ in comparison to (Ga,Mn)As is more than one order of magnitude smaller. Temperature fluctuations have a much bigger influence on the ADMTP measurements in Co$_2$FeAl films and disturb the measurements significantly, so that $V_{\text{therm., long}}$ measured for increasing and decreasing $\varphi$ shows a completely different behavior.

![Figure 4.9: Longitudinal thermoelectric voltage plotted versus the rotation angle $\varphi$ in the 80 nm thick Co$_2$FeAl film, at room temperature (300 K) and at a field of 500 mT. The blue curve is the angle rotation from -30° to 380° and the red curve is the back sweep.](image)

In a recently published article about thermoelectrical measurements in Heusler compounds from Balke et al. [63] a steady-state method using the RZ2001i measurement system from Ozawa science was applied to determine the Seebeck coefficients. Unfortunately
the group did not investigate Co$_2$FeAl, but measured the Seebeck coefficient at 300 K for other similar Heusler alloys: Co$_2$MnAl, Co$_2$MnSi and Co$_2$FeSi. All three materials have negative Seebeck coefficients of $-3 \ldots -10 \mu V/K$ at a temperature of 300 K. We can confirm the negative value for the Seebeck effect in Co$_2$FeAl. In our measurements we established a temperature difference of $\sim 14$ K (the copper blocks had a temperature difference of $\sim 19$ K) and got $\alpha_{\text{long}} \sim \frac{35 \mu V}{K} = 6.8 \frac{\mu V}{K}$ for the Seebeck coefficient, which is in good agreement to Balke et al. [63].

### 4.4 Conclusions and Outlook

In this chapter, we described the successful assembly of a new caloritronic measurement setup and carried out ADMTP measurements in (Ga,Mn)As thin films. We showed that the thermoelectric voltages are proportional to the heater power output and to the thermal gradient so that we can measure the Seebeck coefficient quantitatively. We confirmed that the Seebeck coefficient of (Ga,Mn)As is positive and depends on the angle between the magnetization and temperature gradient. The relative longitudinal thermopower of 7.5% at 10 K (magnetic field 1 T) is similar to the value published by Pu et al. [56]. In contrast to Pu et al. we did not see a saturation behavior for $V_{\text{therm, long}}$ although we conducted AMR measurements up to 7 T. Especially in the B374 sample a quite large asymmetry was observed which could be due to an unwanted out-of-plane contribution due to a not perfectly horizontally aligned sample in the dipstick head.

In our ADMTP measurements the axes of the cubic anisotropy, caused by the crystal symmetry, were slightly shifted ($\sim 5^\circ$) which is not an alignment problem of the sample but already present in the free energy surface of the measurements. The shift is caused by the uniaxial $B_{\bar{1}10}$ anisotropy [59]. Furthermore we approve the presence of a further uniaxial anisotropy parameter $B_{100}$ in the direction of the easy cubic axis in both (Ga,Mn)As samples reported also by Pappert et al. [59]. The origin of both in-plane uniaxial parameters is still under discussion [61, 21, 60, 54]. The different sign of $B_{\bar{1}10}$ we got for the (Ga,Mn)As films is related to the different hole concentration in the samples investigated by Sawicki et al. [21].

Furthermore, we discussed the influence of the new $S_C$ parameter in transverse thermoelectrical voltage signal, arising from the phenomenological Seebeck theory. We concluded that for the presented $ip$ measurements of both (Ga,Mn)As samples the parameter is not absolutely necessary. Only out-of-plane measurements, where the influence of the $S_A$ and
$S_B$ parameters might be seen, will be able to show if the new phenomenological Seebeck tensor theory is needed to describe the experimental data.

In our ADMTP experiment in Co$_2$FeAl we could confirm that the thermopower is negative $\alpha < 0$, but could not resolve M-orientation induced changes. This was to be expected, since $\frac{\Delta \rho}{\rho} = 0.11\%$ in Co$_2$FeAl, so that $\frac{\Delta \alpha}{\alpha} \approx 0.3\%$ which is below the resolution of the current setup. Thus improvements in the caloritronics setup are needed or other Heusler compounds with a larger magneto-Seebeck effect have to be investigated to successfully perform ADMTP measurements.

Nevertheless, our results demonstrate that the newly designed and assembled caloritronics setup works well, and in particular allows for the study of ADMTP in (Ga,Mn)As. Further experiments will imply the construction of a new sample holder allowing us to conduct out-of-plane experiments where it will be possible to study the influence of the other new Seebeck parameters $S_A$ and $S_B$ in the ADMTP measurement.
Chapter 5

Fabrication of Heusler Targets and Films

In the pulsed laser deposition (PLD) chamber of the Walther-Meißner-Institute only oxide films have been grown yet. In the past 5 years some groups reported growth of high quality Heusler thin films by PLD [7, 8, 9, 10]. With respect to the generally used fabrication methods of Heusler thin films, DC/RF sputtering and molecular beam epitaxy (MBE), the PLD growth offers the possibility to easily adjust the growing parameters and in situ change the target materials for multi-layer growth. The disadvantages are the low growth rates (only for Heusler alloys), small sample sizes and the high ablation thresholds for Heusler targets [8]. Nevertheless, one goal of this diploma thesis was to successfully fabricate polycrystalline Heusler targets for the PLD process and grow thin films. Afterwards the films were analyzed by x-ray diffraction (XRD) and superconducting quantum interference device (SQUID) measurements to investigate their magnetic and structural properties and compare them to the Heusler films from the university of Bielefeld grown by sputtering. Due to a lack of time not all properties could be investigated in detail and not all comparisons could be made.

5.1 Fabrication of the Heusler Co$_2$MnSi and Co$_2$FeAl Targets

We selected Co$_2$MnSi and Co$_2$FeAl as the target material systems to fabricate, because they are well known Heusler compounds and have been investigated and fabricated with PLD by various groups so that many growth parameters are available for comparison (e.g. Wang et al. [7]). A. Bauer from chair E21 (TUM) helped us to fabricate polycrystalline
Heusler samples using their induction furnace (see Fig. 5.1) supplied with a high frequency (HF) generator. As source materials we used high purity Co, Mn, Si, Fe and Al in pieces, slugs or pellet form (the purity quality of the materials was at least 3N5, i.e. 99.95% quality). Mn oxidizes within minutes at air. This oxidation can be prevented by melting and casting the Mn into crystalline rods in the copper crucible of the furnace. This was done several times to remove dirt and slag and to improve the purity of Mn. Co, Fe and Al were put into different acids to remove the oxide layer from the surface of the material. The elements were weighted afterwards in stoichiometric 2:1:1 amounts and put into the crucible mold in the induction furnace. After a vacuum pressure of $5.6 \cdot 10^{-7}$ mbar was reached in the furnace chamber, high purity Ar gas (6N) was flooded into the apparatus ($p \approx 2$ bar) and the melting process was started. The Ar gas enables the melting of elements with high vapor pressure, for example Mn. To prevent the melted material to react with the copper crucible, it must be constantly water cooled.

The material in the crucible was melted, cooled and flipped over 4–5 times to improve the intermixing of the elements, always paying attention that the induction field is increased and decreased very slowly. During the cooling process, the surface of Co$_2$MnSi burst several times throwing small parts of the material into the furnace chamber, whereas during the fabrication of Co$_2$FeAl, no cracking took place. We suppose that the reason is the lower hardness of Co$_2$MnSi in comparison to Co$_2$FeAl which leads to a higher bursting probability of the material. More detailed information about the induction furnace and the whole fabrication process can be found in the diploma thesis of A. Bauer [64].

![Figure 5.1: Picture of the inside of the induction furnace: the induction coil is wrapped around the crucible in which the melting and fabrication of the polycrystalline samples takes place (picture taken from [64])](image-url)
After the fabrication the Heusler polycrystals were drop-form shaped and had to be cut into disks with $\sim 2$ cm diameter and 0.5 cm thickness to fit into the target holders for the PLD chamber. The cutting was done using the wire electrical discharge machining (WEDM) technique, in which electrical discharges (sparks) erode the material. A detailed description about this processing method can be found in an article of Ho et al. [65].

### Energy Dispersive X-Ray Spectroscopy Measurements of the Targets

In order to investigate the composition of the Heusler targets (the cut disks) we used energy dispersive x-ray spectroscopy (EDX). In this measurement technique a high-energy beam of electrons is focused on the target surface. The beam kicks out electrons in the inner shells of the hit atoms and the now free, energetically favorable places are reoccupied by other electrons from the outer shells. The energy, which is set free during these transitions, is emitted in form of x-ray photons, which are counted in an energy-resolved detector. The latter are characteristic for the each element.

![Energy Dispersive X-Ray Spectroscopy Measurement](image)

**Figure 5.2:** Typical EDX measurement graph where the pulses = counts of x-rays are plotted versus the emitted x-ray energy for $\text{Co}_2\text{MnSi}$ target.

We analyzed both targets with EDX and chose for the PLD process the side of the target disk where the composition was closer to our aimed composition of 50:25:25 for $\text{Co}_2\text{MnSi}$ and $\text{Co}_2\text{FeAl}$. In Fig. 5.2 a typical EDX measurement graph is depicted where the pulses, i.e. the number of detected x-rays, versus the energy of the x-rays is plotted. We measured at 7 different positions on the target surface starting from one edge, going then to the center of the disk and proceeding further to the opposite edge. In Fig. 5.2 the measurement
at the first position near the edge is shown for the Co$_2$MnSi target. From the specific transition energies for the elements an algorithm calculates the percentage of the elements found in the investigated area. In Tab. 5.1 these single element contributions are shown for all 7 different measurement positions for both target. Here only measurements for the smaller sides of the target disks are presented, whose compositions are closer to the ideal value (the other data can be found in the appendix A.2). We observe that the composition of the Co$_2$MnSi target is very close to the aimed composition, whereas in Co$_2$FeAl there is a slight excess of Co and Fe and a deficit of Al at (almost) all measured positions. This leads to the question where the missing aluminum went. As stated above, during the melting process in the furnace, no material was lost in the case of Co$_2$FeAl. An investigation reveals that in the remaining parts of the cut polycrystal, especially at the surface, a large excess of Al can be found. Hence, the diffusion and convection processes taking place in the metallic fluid during the melting process in the furnace could be the reason for the Al excess at the surface (Al has the lowest density out of the three materials).

All in all we could successfully fabricate both Heusler targets and the stoichiometry of the compounds is also in good agreement with the aimed values for the composition.

<table>
<thead>
<tr>
<th>Co$_2$MnSi</th>
<th>1. pos.</th>
<th>2. pos.</th>
<th>3. pos.</th>
<th>4. pos.</th>
<th>5. pos.</th>
<th>6. pos.</th>
<th>7. pos.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>50.13 %</td>
<td>50.00 %</td>
<td>50.48 %</td>
<td>49.95 %</td>
<td>50.22 %</td>
<td>50.46 %</td>
<td>49.73 %</td>
</tr>
<tr>
<td>Mn</td>
<td>24.22 %</td>
<td>25.06 %</td>
<td>25.96 %</td>
<td>25.09 %</td>
<td>24.88 %</td>
<td>25.08 %</td>
<td>25.31 %</td>
</tr>
<tr>
<td>Si</td>
<td>25.66 %</td>
<td>24.94 %</td>
<td>23.56 %</td>
<td>24.97 %</td>
<td>24.90 %</td>
<td>24.47 %</td>
<td>24.96 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Co$_2$FeAl</th>
<th>1. pos.</th>
<th>2. pos.</th>
<th>3. pos.</th>
<th>4. pos.</th>
<th>5. pos.</th>
<th>6. pos.</th>
<th>7. pos.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>50.98 %</td>
<td>51.05 %</td>
<td>51.31 %</td>
<td>51.16 %</td>
<td>50.98 %</td>
<td>50.86 %</td>
<td>50.77 %</td>
</tr>
<tr>
<td>Fe</td>
<td>26.13 %</td>
<td>26.29 %</td>
<td>26.91 %</td>
<td>26.85 %</td>
<td>26.54 %</td>
<td>26.79 %</td>
<td>26.08 %</td>
</tr>
<tr>
<td>Al</td>
<td>22.89 %</td>
<td>22.67 %</td>
<td>21.78 %</td>
<td>21.99 %</td>
<td>22.49 %</td>
<td>22.35 %</td>
<td>23.15 %</td>
</tr>
</tbody>
</table>

**Table 5.1**: Calculated percentage of the elements found at the 7 different positions (pos.) on the targets. An ideal full-Heusler has the element composition ratio of 50:25:25. The first measurement area is at one edge of the target, the next closer to the center and so on. The last measurement is carried out at the opposite edge of the target. Here the analysis was done for the *smaller* sides of the targets.
5.2 Growth of Co₂MnSi Thin Films

The next and last step towards the fabrication of Heusler thin films is the PLD process. In this growing method, material of a target is ablated and epitaxially deposited on the surface of a substrate, which should match the lattice parameters of the target (cf. Fig. 5.3). Further information about the PLD process and the equipment can be found in the diploma theses of A. Brandlmaier and Ph.D. A. Boger [66, 67].

![Schematic sketch of the PLD process](image)

**Figure 5.3:** Schematic sketch of the PLD process (taken from [68])

To control the growth temperature an IR-laser (λ=938 nm, P = 140 W) and for the target ablation a KrF-Excimer laser (ComPexPro201, Lambda Physik) with a wavelength of λ = 248 nm is used, emitting up to 600 mJ/pulse at a repetition rate of 1–10 Hz. We used 5 × 5 mm² MgO (100) substrates (CrysTec) which were polished on the film growth side and coated with a thin Pt layer (∼ 50 nm) on the back side (via sputtering) to improve the thermal coupling to the IR-laser. MgO has a fcc-lattice structure with a lattice constant of $a_{\text{MgO}} = 4.212$ Å [69]. Co₂MnSi ($a_{\text{Co₂MnSi}} = 5.65$ Å [70]) and Co₂FeAl ($a_{\text{Co₂FeAl}} = 5.64$ Å [71]) are grown under 45° on the substrate (diagonal length: $\sqrt{2}a_{\text{MgO}} = 5.80$ Å) to reduce the lattice mismatch to 5.7% (cf. Fig. 3.1). The distance between target and substrate was (60±1) mm for all grown Heusler films. The pressure in the UHV (ultra-high-vacuum) PLD chamber was always around 4 × 10⁻⁸ mbar. We started with the thin film growth of Co₂MnSi because a lot of groups reported on successfully growing this Heusler compound by PLD (e.g. [7, 8, 11, 9]) and their growth parameters are a good reference and starting
point for our film growth. Since my colleagues were afraid of polluting the whole chamber with ablated Heusler material (we did not know how big the plasma plume would be), the first films were grown in Argon atmosphere with a pressure of \( p = 0.3 \ldots 0.7 \mu \text{bar} \). The substrate temperature was 500°C and the target was shot by 10000 Excimer laser pulses (400 mJ/pulse) with an energy density of \( 4 \text{J/cm}^2 \) at a repetition rate of 2 Hz. The pulses were sent in 100 bursts of 100 pulses with a waiting time of 20 s between two bursts, granting enough relaxing time for the atoms to reorder themselves epitaxially on the substrate surface.

It turned out that the plasma plume was very small and thus only little Co\(_2\)MnSi material was deposited on the substrate. With the naked eye one could hardly see a difference to the untreated substrate. Even XRD (x-ray diffraction) measurements did not show any film reflection, only the substrate reflections were visible (details can be found in the XRD section on page 83). To enlarge the plasma plume the further films were grown in UHV (ultra high vacuum) without an inert gas atmosphere. This led to the first films on which we could clearly see the shimmering metallic film layer and film reflections in the XRD measurements. In the final step we optimized the growth for Co\(_2\)MnSi by varying the growth temperature (320...600°C), the number of pulses (10000...100000) and energy density (1...4 J/cm\(^2\)). An overview of all grown films including the different growth parameters can be found in Tab. 5.2. The discussion about the quality and growth parameters of the Co\(_2\)MnSi films is presented in the next chapter.

Unfortunately there was not enough time to determine the optimum growth parameters of Co\(_2\)FeAl. Therefore we only fabricated one single test-film of Co\(_2\)FeAl applying the best growth parameters found in Co\(_2\)MnSi. During the growth process the plasma plume was much smaller in comparison to Co\(_2\)MnSi, which already indicated that only little material was deposited onto the substrate. On the surface of the Co\(_2\)FeAl thin film, only a slight metallic shimmer was visible - the film was nearly transparent - which leads to the conclusion that the energy of the KrF laser was not high enough. Thus for the future growth of Co\(_2\)FeAl there are different possibilities to increase the amount of material deposited onto the substrate: on the one hand we could increase the energy flux (energy per pulse) of the excimer laser or on the other hand reduce the distance between target and substrate.

**Reflection High Energy Electron Diffraction** To monitor and characterize the growth process a RHEED (reflection high energy electron diffraction)-system was used. A high energetic electron beam hits the surface of the sample under an angle of 1°-4°. Due to the
small angle the electron beam is only diffracted at the upper atom layers of the sample. Then the diffracted beam reaches a fluorescence screen on which an interference pattern becomes visible. A CCD-camera is monitoring this image constantly. The epitaxial growth leads to an oscillating RHEED signal out of which the growth rate can be extracted. More details can be found in [66, 72]. Due to the limited space in this diploma thesis, we skip the presentation and discussion of the RHEED images from our growth of Co$_2$MnSi.
Table 5.2: Summary of the Heusler thin films with their different growth parameters. For all films the energy per pulse was 450 mJ. a) indicates that the determination of the film thickness was not possible by the simulation program Leptos.
5.3 Characterization of the Grown Thin Films

For the characterization of the grown \( \text{Co}_2\text{MnSi} \) thin films XRD-measurements were carried out to investigate the structural quality, EDX-measurements to analyze the composition of our films, SQUID measurements to get information about the magnetic properties of the films and microscope images to examine the amount and size of droplets on the film surface. Furthermore the quality between our PLD grown \( \text{Co}_2\text{MnSi} \) films and the sputtered \( \text{Co}_2\text{MnSi} \) films from the university of Bielefeld was compared.

5.3.1 X-Ray Diffraction Measurements and Surface Analysis via Microscope Images

The structural properties of our grown \( \text{Co}_2\text{MnSi} \) thin films were studied by x-ray diffraction (XRD). In this technique monochromatic x-rays are sent under a specific angle of incidence \( \theta \) onto the sample surface where they are deflected and afterwards detected (cf. Fig. 5.4).

![Setup of a four-circle-x-ray-diffractometer](image)

**Figure 5.4:** Setup of a four-circle-x-ray-diffractometer. The four independent angles are \( 2\theta, \omega, \chi \) and \( \varphi \). When Bragg’s law is fulfilled the incident and deflected beam angles are both \( \theta \), as shown in the sketch (taken from [66]).

Only when the optical path difference between the incident beam and the deflected beam is a multiple integer value \( n \) of the wavelength \( \lambda \), the interference is constructive:
Here \( d \) is the distance between two lattice planes on which the x-rays are deflected and \( n \) is the order of diffraction. Eq. (5.1) is commonly known as Bragg’s law.

The used XRD system is a 4-circle-diffractometer (Bruker AXS, D8-Discover) where the sample plate can be rotated in all directions. A Goebel-mirror parallelizes the x-rays so that effectively the intensity of the beam is increased by a factor of ten. The monochromator blocks the Cu-K\(_{\alpha 2}\)-line and thus only the Cu-K\(_{\alpha 1}\)-line with a wavelength of \( \lambda_{\text{Cu-K}_{\alpha 1}} = 154.056 \text{ pm} \) [73] passes. The software EVA and Leptos (Bruker company) is used to analyze the data from the detector.

We now briefly describe the measurement methods we used:

**\( \theta - 2\theta \)-Scans** We use this method to detect and compare the intensities of the different film reflections, here the (200) and (400) Co\(_2\)MnSi reflections. The angle \( \omega \) of the sample plate is rotated continuously while the detector is moved at twice the speed in order to keep the angle \( 2\theta \) between detector and x-ray source constant. Therefore always when Bragg’s law (Eq. (5.1)) is fulfilled, we get a maximum of intensity. This is the case when \( \frac{d}{n} \text{ (} n = 1, 2, \ldots \text{)} \) equals the lattice constant of the substrate or the film.

**Rocking Curves** This is one method of determining the crystalline quality of thin films. Here the position of the detector \( 2\theta \) is fixed at an angle where Bragg’s law is fulfilled for a special lattice plane. In the scan the sample is slightly rotated around the \( \omega \)-axis. If the sample consists of many crystallites which are slightly differently oriented, Bragg’s law is fulfilled for more than one value of \( \omega \), which leads to a broad curve. The FWHM (full width at half maximum) of the resulting rocking curve is a measure for the mosaic spread of a sample.

**X-Ray Reflectometry** The reflectometry offers a method to determine the thickness and the roughness of interfaces of a film. Here the x-rays are sent in a very small angle \( \theta \) (slightly larger than the angle of total reflection) onto the film in order to reflect at the surface as well as at the interfaces between film and substrate. The x-rays reflected at the surface of the film and the substrate interfere constructively or destructively, but have different intensities, leading to maxima and minima on the exponentially decreasing intensity signal. The film thickness can be determined from
the period of oscillations by a special fitting program (Leptos) and the exponential
decrease of the signal of reflectometry yields information about the roughness of the
film surface.

Further and more detailed information about XRD and the different measurement meth-
ods can be found in the diploma theses of Ph.D. A. Boger, S. Bauer and A. Brandlmaier
[66, 67, 72]. The values for the film thicknesses, achieved by a simulation via the program
Leptos, can be found in Tab. 5.2.
For examining the surface of the films, especially the concentration and size of droplets,
a LEICA DM LM microscope was used. All of our images presented in this thesis were
taken at a magnification of 50x.

Temperature Series of Co$_2$MnSi Films Using a constant Excimer laser energy (50000
pulses at 10 Hz with an energy density of 4 J/cm$^2$), we have grown Co$_2$MnSi thin films at 4
different growth temperatures, 320 °C (ACMS 08), 400 °C (ACMS 05), 500 °C (ACMS 04)
and 600 °C (ACMS 07) in UHV. First we want to compare the XRD measurements for
the 4 films. In Fig. 5.5(a) the intensities (in counts per second) for the $\theta - 2\theta$-scan from
20° to 110° are shown. The two MgO substrate reflections (200) and (400) are clearly
visible for all growth temperatures and are at the positions $2\theta = 42.9°$ and $2\theta = 94.0°$
which are in good agreement with the literature values. When comparing the Co$_2$MnSi
(200) and (400) film reflections for the four growth temperatures we observe that only
the 400 °C (red) and 500 °C (green) samples show distinct peaks. Especially when taking
a closer look at Fig. 5.5(b), where the yellow area of Fig. 5.5(a) with the Co$_2$MnSi (400)
film reflection is depicted. Here the red curve shows the largest signal which also matches
the literature value of 65.92° (violet) very well.
Analyzing the reflectometry data in Fig. 5.5(c) we see that the blue curve (600 °C) de-
creases the fastest and shows no oscillations at all, which means the film is extremely
thin. In fact we assume that at this high growth temperature the atoms of Co$_2$MnSi
diffuse into the substrate and no Heusler compound is formed. We also did not observe
any film reflection in Fig. 5.5(a) and (b). The film grown at 320 °C shows the best surface
structure indicated by the clearly visible oscillations up to $2\theta = 4°$. The second best film
concerning surface roughness is the 400 °C film (red) followed by the 500 °C film (green).
Summarizing the XRD measurements of the growth temperature series one can clearly
say that the 400 °C film shows the best structural characteristics. This establishes 400 °C
as the optimum growth temperature.
Figure 5.5: Comparison of a Co$_2$MnSi film series grown with a constant energy density (of the KrF-laser) of 4 J/cm$^2$ at 4 different temperatures: 320 °C (black), 400 °C (red), 500 °C (green) and 600 °C (blue). (a) shows a $\theta - 2\theta$-Scan with the indicated film and substrate reflections, (b) the Co$_2$MnSi (004) film reflection and the literature value 65.92° (violet) and (c) the reflectometry data.

Taking a quick look at the microscope images (50×magnification) in Fig.5.6 for the Co$_2$MnSi film temperature series we observe that the higher temperature films show less droplets than the films grown at lower temperatures. In general, the reason for the generation of droplets during the PLD process is the UHV, where fast and large particles can travel without being scattered to the substrate, leading to inhomogeneities and droplets. When an inert gas atmosphere is used instead, these particles are mostly scattered away. At low temperatures the large particles and droplets do not merge with the Co$_2$MnSi lattice at the surface.
Energy Density Series of Co$_2$MnSi films  Having found 400°C as the optimum growth temperature the next growth parameter we optimized was the energy density (of the Excimer laser). Apart from this laser fluence, the other growth parameters were not changed and stayed the same as in the temperature series. In Fig. 5.7 the same XRD plots as for the temperature series are shown for the different fluences of 1 J/cm$^2$ (ACMS 12 in black), 2 J/cm$^2$ (ACMS 11 in red), 3 J/cm$^2$ (ACMS 09 in green) and 4 J/cm$^2$ (ACMS 05 in blue). In Fig. 5.7(a) both substrate reflections are clearly visible for all laser fluences, whereas for the film reflections differences can be seen. In Fig. 5.7(b) the Co$_2$MnSi (400) film reflections for the different energy densities are shown. The film with the highest fluence (4 J/cm$^2$) has the largest peak, followed by the green curve (3 J/cm$^2$) and the slightly shifted red curve (2 J/cm$^2$), which has its maximum further away from the literature value. The film with an energy density of 1 J/cm$^2$ has no film reflection signal. A comparison of the surface roughness in the reflectivity measurements (Fig. 5.7(c)) reveals that the films with the fluences of 2 J/cm$^2$ and 3 J/cm$^2$ show the best and nearly identical results. The black curve (1 J/cm$^2$) shows only one oscillation and is thus very thin, not even showing
any film reflections. The blue curve has a higher oscillation rate, is thus thicker than the other films, but the surface roughness is slightly higher in comparison with the red and green curves. All in all the best energy based on the XRD measurements is $4 \ J/cm^2$.

![Figure 5.7](image)

Figure 5.7: Comparison of a Co$_2$MnSi films series grown at 4 different energy densities: $1 \ J/cm^2$ (black), $2 \ J/cm^2$ (red), $3 \ J/cm^2$ (green) and $4 \ J/cm^2$ (blue) at a temperature of $400^\circ C$. (a) shows a $\theta - 2\theta$-Scan with the indicated film and substrate reflections, (b) the Co$_2$MnSi (004) film reflection and the literature value 65.92$^\circ$ (violet) and (c) the reflectometry data.

If we now investigate the morphology of the film surfaces by microscope images taken with a magnification of 50x, we observe in Fig. 5.8 that only the film with a laser fluence of $4 \ J/cm^2$ is covered with lots of large droplets in comparison to the other three films. This strictly argues against the use of a fluence of $4 \ J/cm^2$ for the further film growth of Co$_2$MnSi. Combining this result with the results from the XRD measurements yields that the best compromise is an energy density of $3 \ J/cm^2$. 
Section 5.3
Characterization of the Grown Thin Films

(a) ACMS 12; 1 J/cm²  
(b) ACMS 11; 2 J/cm²  
(c) ACMS 09; 3 J/cm²  
(d) ACMS 05; 4 J/cm²

Figure 5.8: Microscope images (50× magnification) of the film surfaces of the Co₂MnSi energy density series ((a) 1 J/cm², (b) 2 J/cm², (c) 3 J/cm² and (d) 4 J/cm²). The growth temperature was 400 °C for all 4 films.

After optimizing the growth temperature and laser fluence for Co₂MnSi we now compare our best film (ACMS 14), grown with 100000 pulses, with one comparable sputtered Co₂MnSi film from the university of Bielefeld (CMS 04). The latter was sputtered at 400 °C and in situ annealed for 1 hour at the growing temperature. Figure 5.9 presents the XRD data with our self-grown sample ACMS 14 in blue and Bielefeld sample in red. In Fig. 5.9(a) a θ – 2θ-Scan shows the same positions for the substrate reflections, but not for the film reflections. In Fig. 5.9(b) the different positions of the Co₂MnSi reflection (400) in the two films can clearly be observed. Both peaks are slightly shifted in comparison to the literature value of 65.92°, which could be due to the different growing techniques, the annealing process of the Co₂MnSi film from Bielefeld or the relatively high lattice mismatch of 5.7% between Co₂MnSi and MgO. The diagonal of MgO (d = √2a = 5.80 Å) is larger than the lattice constant of Co₂MnSi (a = 5.65 Å), which leads to an extension (strain) of the Co₂MnSi lattice in the film plane. If a constant volume is assumed the film gets compressed in the z-direction (growth direction). To hit the same spot on the sample surface a larger diffraction angle is needed which leads to a shift of the 2θ angle towards
larger angles. This reasoning speaks in favor of the Bielefeld film, whose Co$_2$MnSi (400) reflection is in comparison to the literature value at a slightly larger angle.

![XRD measurement comparison](image)

**Figure 5.9:** XRD-measurement comparison of our best PLD-grown Co$_2$MnSi film (ACMS 14) in blue with the at 400 K sputtered and annealed 20 nm Co$_2$MnSi film (CMS 04) in red. In (a) a $\theta-2\theta$-Scan with the indicated film and substrate reflections and in (b) a close up view of the Co$_2$MnSi reflection (400) is shown, including the literature value of 65.95° (black). In (c) the reflectometry data of both films can be seen, revealing that both films have nearly the same thicknesses.

Nevertheless the blue reflection of the Bielefeld sample has nearly twice the number of counts than the red reflection; for the Co$_2$MnSi reflection (200), it is the opposite, but the counts per second rate is for both smaller than 4. The reflectivity measurement in Fig.5.9(c) reveals that both films nearly have the same thicknesses (21.4 nm for the WMI film and 20.2 nm for the Bielefeld film), but the surface quality of the Co$_2$MnSi film from Bielefeld is much better, showing a slower decay of the intensity and more
distinctive oscillations. The reason for this behavior must be the annealing process where the surface atoms have time to realign in the lattice crystal structure leading to a better surface quality and less roughness.

In Fig. 5.10 the rocking curves of the Co$_2$MnSi (400) reflection can be observed for both samples. The blue curve has a significantly higher intensity and the FWHM is about a factor 2 smaller. This means the mosaic spread of the CMS 04 film is higher, i.e. more different orientations of the crystallites, indicating that the WMI film has a slightly better quality. Kubota et al., who has grown 30 nm Co$_2$MnSi thin films on MgO (100) with a Cr-buffer layer by sputtering, measured a rocking curve FWHM of 1.25° for the Co$_2$MnSi (400) reflection [74]. Thus our film is also competitive with those of other groups.

Summarizing the comparison results for both films, we conclude that the structural quality of our PLD-grown film is at the same level or slightly higher than the Co$_2$MnSi film from Bielefeld. Only the surface quality is significantly worse in our thin film which could most likely be improved by annealing.

![Figure 5.10](image.png)

**Figure 5.10:** Comparison of rocking curves of the Co$_2$MnSi (400) reflection between the WMI (blue) and Bielefeld (red) Co$_2$MnSi films ACMS 14 and CMS 04. The blue curve shows a higher peak and smaller FWHM, indicating a smaller mosaic spread.

### 5.3.2 Energy Dispersive X-Ray Spectroscopy Measurements in Co$_2$MnSi Films

We now investigate the composition of the Co$_2$MnSi film by EDX-measurements. The EDX technique was explained on page 77. We made measurements in 5 areas beginning at one edge of the film, going through the middle (position 3) and ending at the opposite film...
edge. In Tab. 5.3 the results of the EDX measurements are found. The most interesting
fact is that there is a relatively large excess of Si found in the film and a deficit of mainly Co
and a bit Mn. EDX measurements in other $\text{Co}_2\text{MnSi}$ films reveal the same characteristic.
Hence, during the growth process unknown effects lead to a loss of Co (and Mn) or the
target composition changed due to the ablation of deeper layers. Therefore the next step
would be to investigate the target again at the circular notch, where the ablation took
place. Nevertheless, this is surprising because of the good structural qualities and film
reflections of this $\text{Co}_2\text{MnSi}$ sample. We have not done any EDX measurements on the
Bielefeld thin films, yet, which is planned for the future.

<table>
<thead>
<tr>
<th>$\text{Co}_2\text{MnSi}$</th>
<th>1. position</th>
<th>2. position</th>
<th>3. position</th>
<th>4. position</th>
<th>5. position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>46.01 %</td>
<td>42.68 %</td>
<td>44.92 %</td>
<td>45.51 %</td>
<td>40.42 %</td>
</tr>
<tr>
<td>Mn</td>
<td>24.28 %</td>
<td>31.26 %</td>
<td>21.89 %</td>
<td>23.23 %</td>
<td>23.68 %</td>
</tr>
<tr>
<td>Si</td>
<td>29.72 %</td>
<td>26.07 %</td>
<td>33.19 %</td>
<td>31.26 %</td>
<td>35.90 %</td>
</tr>
</tbody>
</table>

Table 5.3: Calculated percentage of the elements found at the surface of the $\text{Co}_2\text{MnSi}$ sample ACMS 14 at 5 different positions. The ideal composition of the full-Heusler alloy has the element ratio 50:25:25. The first measurement area is at one edge of the film, the next closer to the center and so on. The last measurement is carried out at the opposite edge.

5.3.3 Superconducting Quantum Interference Device Measurements

The magnetic properties of two $\text{Co}_2\text{MnSi}$ samples, which show the best structural qualities, are investigated by SQUID (superconducting quantum interference device) measurements using the SQUID device from Quantum Design (model: MPMS XL-7). During the measurement a diamagnetic polythene straw in which the thin film sample is glued, is constantly moved up and down through a superconducting pick-up coil (a second order gradiometer). The moving sample changes the flux in the pick-up coil leading to a proportional current. A RF-SQUID (radio-frequency-SQUID) transforms the current into a voltage signal which can be used to calculate the magnetization of the sample (accuracy $10^{-8}$ emu = $10^{-11}$ J/T). A superconducting magnet, which contains the gradiometer, can generate external fields up to 7 T. More details about this technique and the RF-SQUID can be found in the diploma thesis of S. Bauer [72].

The two samples investigated are ACMS 14 and 04 which show a completely different behavior in the $M(H)$ plot in Fig. 5.11 (details about the growth parameters of these films can be found in Tab. 5.2). The diamagnetic contribution of the substrate was already
subtracted from the measured data in the plot. The 21.4 nm thick sample with a coercive field of 5.5 mT shows a much smaller hysteresis loop than the 28.7 nm thick sample ($H_c = 41.8$ mT).

The reasons are probably the completely different growth parameters for those films. D. Erb reported also about different hysteresis curves of sputtered Co$_2$MnSi films, where the as-prepared films showed a larger hysteresis ($H_c \approx 10$ mT) in comparison to the annealed films ($H_c \approx 1$ mT) [75].

![Figure 5.11: SQUID measurement of $M(H)$ at a temperature of 50 K for the Co$_2$MnSi films ACMS 04 and ACMS 14 (details about the growth parameters of these films can be found in Tab. 5.2).](image)

There is a factor of 10 difference between the coercive fields, similar to our two films;

<table>
<thead>
<tr>
<th>ACMS 14</th>
<th>$M_S(\mu_B/\text{f.u.})$</th>
<th>$M_{\text{remanence}}(\mu_B/\text{f.u.})$</th>
<th>$H_{\text{coercive}}$(mT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 K</td>
<td>5.34</td>
<td>4.52</td>
<td>7.90</td>
</tr>
<tr>
<td>15 K</td>
<td>5.28</td>
<td>4.47</td>
<td>7.24</td>
</tr>
<tr>
<td>50 K</td>
<td>5.45</td>
<td>4.40</td>
<td>5.50</td>
</tr>
<tr>
<td>300 K</td>
<td>5.22</td>
<td>4.28</td>
<td>2.68</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ACMS 04</th>
<th>$M_S(\mu_B/\text{f.u.})$</th>
<th>$M_{\text{remanence}}(\mu_B/\text{f.u.})$</th>
<th>$H_{\text{coercive}}$(mT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 K</td>
<td>4.34</td>
<td>3.95</td>
<td>42.45</td>
</tr>
<tr>
<td>50 K</td>
<td>4.92</td>
<td>3.86</td>
<td>41.83</td>
</tr>
<tr>
<td>300 K</td>
<td>4.73</td>
<td>3.55</td>
<td>31.28</td>
</tr>
</tbody>
</table>

Table 5.4: Summary of the most important magnetic parameters, the saturation magnetization, the remanence and coercive field, for the Co$_2$MnSi films ACMS 14 and ACMS 04 at different temperatures (5, 15, 50 and 300 K).
but we did not anneal the two investigated films. For our ACMS 14 sample (blue curve) the saturation magnetization $M_S = 5.45 \mu_B$/f.u. is larger than the literature value of $5.07 \mu_B$/f.u. [70], whereas for the ACMS 04 sample (black curve) the value is closer to the literature value ($M_S = 4.92 \mu_B$/f.u.). In Tab. 5.4 the magnetic parameters (the saturation magnetization, the remanence and coercive field) of both films for different temperatures are shown. For all temperatures $M_{\text{remanence}}$ and $M_S$ are larger for the ACMS 14 film.

5.3.4 Conclusion and Outlook

In this chapter the successful fabrication of the two Heusler Co$_2$MnSi and Co$_2$FeAl polycrystals in the induction furnace was described, out of which the targets were cut by wire electrical discharge machining. EDX measurements showed that the composition of the targets is close to the aimed ideal value. The targets were used for thin film growth by PLD under UHV conditions. We concentrated our efforts on Co$_2$MnSi and optimized the growth temperature and energy density to improve the film quality. The grown films were investigated by XRD measurements to analyze their structural quality, including film peak height, mosaic spread and thicknesses. Microscope images yielded information about the surface texture of the films, especially about the size and amount of droplets. EDX measurements showed a deficit of Co in the investigated films and revealed an excess of Si. Here one has to find out if the growth process or the target is the reason for this issue. SQUID measurements revealed that the saturation magnetization $M_S = 4.92 \mu_B$/f.u. and respectively $M_S = 5.45 \mu_B$/f.u. at 50 K agrees well with the literature value of $5.07 \mu_B$/f.u.. At last we showed that the structural qualities of our PLD grown films are the same or even better as the sputtered Co$_2$MnSi films from the university of Bielefeld, apart from the surface roughness which is much better in the Bielefeld films due to their performed annealing process. The FWHM of the rocking curve is 0.86° for our film whereas in the CMS 04 film from Bielefeld the value is 1.49°, indicating that the mosaic spread is larger in the latter film.

Due to the lack of time we unfortunately could not perform magnetotransport experiments in the self-grown Co$_2$MnSi films and compare the results with the films from Bielefeld. Furthermore additional SQUID measurements could be carried out to systematically study the influence of the growth parameters onto the magnetic properties. The growth process of Co$_2$MnSi could be most likely further improved by annealing with regard to the surface roughness of the films.
Chapter 6

Conclusion and Outlook

Since about ten years spintronics has aroused more and more interest in the international research community. The goal of spintronics is the utilization of the electronic spins to offer a new degree of freedom in electronic systems. There are various applications which could benefit from controlling the spin. For applications in the commercial sector - magnetic storage applications for example - it is necessary that the magnetic properties of the used materials are reproducible and can be controlled by preferably easy techniques. This is only possible if we have detailed knowledge about the magnetic properties of the materials and how we can control and self-tailor them. Hereby, the control of the magnetization is essential. Without an external field the magnetization is oriented along energetically favorable directions, the easy axes, caused by the magnetic anisotropy. By controlling this anisotropy the magnetization can be influenced. The future goal of the research is to use the magnetic anisotropy for technical applications.

A promising material class for spintronics applications are Heusler compounds. They are theoretically 100% spin polarized. For the two Heusler alloys, Co$_2$FeAl (ADMR) and Co$_2$MnSi (PLD fabrication), we studied in this thesis, a spin polarization of 50 – 60% for low temperatures was reported [15]. Due to their lattice constant matching with the III–V semiconductors, high Curie temperature $T_C$ above room temperature and large bandgap at the Fermi level in general, the Heusler alloys hold great potential for spintronic applications.

To investigate the magnetic anisotropy we used the angle dependent magnetoresistance (ADMR) measurement technique. The advantage of this method is that the magnetic anisotropy can be determined quantitatively by a numerical simulation by fitting experimental data. We also gain the knowledge about the 3D free energy landscape. In this technique the longitudinal and transverse voltages of a patterned Hall-bar sample
are measured at a fixed temperature and a constant magnetic field, as a function of the orientation of this external magnetic field. Knowing the dimension of the Hall-bar the longitudinal and transverse resistivities can be calculated. To understand the behavior of the resistivities a phenomenological model for single crystalline samples is applied which was first used by Birss [29] and McGuire & Potter [30]. Starting point is the development of the resistivity tensor in powers of the magnetization up to the fourth order. By using Neumann’s principle, the symmetry operations of the specific crystal symmetry and the Onsager relation, the resistivity tensor can be simplified. To simulate our measured data with the resistivity tensor model first the free energy has to be minimized to determine the orientation of the magnetization. The free energy includes the Zeeman energy and the different magnetic anisotropy contributions (shape anisotropy, crystal symmetry anisotropy, magneto-elastic anisotropy) which are material dependent. In our Heusler thin films we have a cubic and an uniaxial in-plane anisotropy and an uniaxial anisotropy in out-of-plane direction. By knowing the orientation of the magnetization the longitudinal and transverse resistivities can be calculated. For this numerical simulation, resistivity and anisotropy parameters have to be plugged into the equations which are gained by fitting the measured data.

Furthermore we performed angle dependent magnetothermopower measurements (ADMTP) where instead of an electrical current, a heat current was applied along the Hall-bar of the sample. For these measurements the longitudinal and transverse voltages were also measured at a fixed temperature and a constant magnetic field, for different orientations of the external magnetic field. The same model used for the resistivity can be applied to the Seebeck coefficient $\alpha$ (also called thermopower), which describes the proportionality between a temperature gradient $\nabla T$ and an electric field: $\mathbf{E} = -\alpha \cdot \nabla T$. The only difference is that the Onsager relation only yields a relation between the Seebeck and Peltier tensor and thus does not simplify the Seebeck tensor. So in comparison to the resistivity tensor additional terms can be found in the Seebeck tensor. For the current or the temperature gradient respectively applied in [110] direction there exists one additional term (with parameter $S_A$) in the longitudinal and two additional terms (with parameters $S_B$ and $S_C$) in the transverse thermopower, all of third or fourth order. According to our calculations coefficient $S_B$ should be the largest because it is the only new parameter which does not consist of a difference of $s_i$ parameters (cf. Chpt. 2.3.2). This model applied on the thermopower was never tested before and has to be experimentally verified.
6.1 Angle Dependent Magnetoresistance Measurements in Co$_2$FeAl

We performed ADMR measurements on four Co$_2$FeAl films of different thicknesses ($d = 20, 50, 80$ and $100$ nm) at temperatures of $T = 10, 50, 100, 150, 200, 250, 300, 350$ K and at magnetic fields of $\mu_0H = 20, 40, 200, 500, 1000, 2000$ mT. The films were fabricated by I.-M. Imort at the university of Bielefeld via magnetron sputtering at room temperature. For the growth, first a $5$ nm thick MgO buffer layer was deposited to cover the MgO (001) substrate and to coat surface contaminations. Then, the Co$_2$FeAl film was sputtered on the buffer layer. Its in-plane orientation is rotated by $45^\circ$ with respect to MgO to guarantee an epitaxial growth and reduce the lattice mismatch ($\sim 4.5\%$). The measurements were performed at three different rotation configurations of the external magnetic field: in $ip$ configuration (the film normal $n$ is the rotation axis), in $oopj$ (the current direction $j$ is the rotation axis) and in $oopt$ (the in-plane vector $t$, which is perpendicular to the current density $j$, is the rotation axis). The current was always applied in [110] direction for all measurements.

In the numerical simulation, which is based on the resistivity tensor model, we have fitted the resistivity parameters $\rho_0, \rho_1, \rho_2, \rho_6, \rho_7$ and the anisotropy parameters $B_{\text{cub}}, B_{110}$ and $B_{001}$ so that the simulated curves for $\rho_{\text{long}}$ and $\rho_{\text{trans}}$ match the experimental data. It was sufficient to use parameters up to the second order of magnetization for the fitting process to describe all data very well.

The resistivity parameters were all field independent except $\rho_0$, which is the only resistivity parameter which needs to be $H$ dependent to obtain satisfying fitting results. In the longitudinal resistivity, the parameter $\rho_0$, which is independent of magnetization, is about two orders of magnitude larger than the parameter $\rho_1$ and $\rho_2$. Parameter $\rho_1$ describes the anisotropic magnetoresistance (AMR) and parameter $\rho_2$ the out-of-plane AMR. Furthermore $\rho_0$ is increasing with rising temperature which can be explained by a larger phonon scattering rate. For the anomalous Hall-effect (AHE) parameter $\rho_6$ we discovered that skew scattering [25] is the dominating process, since $\rho_6 \propto \rho_{\text{long}}$.

One crucial result in this work is that we observed a sign change of the planar Hall-effect (PHE) parameter $\rho_T$ for the $80$ nm and $100$ nm thick Co$_2$FeAl films, which occurs between $T = 60$ K and $T = 140$ K. For the two thinner films this behavior did not appear, indicating a thickness dependent phenomenon. One reason could be a structural change in the thicker films. However, the question arises why we did not see any effect of this
structural change in the other parameters. Bowen et al. also observed this sign change of the PHE in Heusler Fe\(_{3+x}\)Si\(_{1-x}\) thin films, but only for films with \(x = 0\), and not for non-stoichiometric samples [49, 50]. Hence, the sign change could be an indicator for good stoichiometry.

The different film thicknesses influence the resistivity parameters (cf. Fig. 3.13), but no reasonable trend can be observed, except for the PHE parameter \(\rho_7\). The reason could be the \(B_2\) structure of our four Co\(_2\)FeAl films where the Fe and Al atoms are disordered, so that the positions of the atoms in the unit cells could be different.

One of the main goals in this thesis was the determination of the anisotropy parameters in Co\(_2\)FeAl using the ADMR measurement method. To our knowledge this is the first quantitative determination of the magnetic anisotropy parameters for Co\(_2\)FeAl. The out-of-plane anisotropy parameter \(B_{001}\) shows the largest value (825 mT) for a temperature of \(T = 10\) K, its lowest (660 mT) for \(T = 350\) K and is linearly decreasing with increasing temperature. \(B_{001}\) is two orders of magnitude larger than the other two anisotropy parameters, \(B_{110}\) and \(B_{\text{cub}}\) and consists of two contributions: the shape anisotropy and the magneto-elastic anisotropy. The calculation of the shape anisotropy contribution \(B_{\text{shape}} = \frac{1}{2}\mu_0M_S\) yields that more than 75\% of the out-of-plane anisotropy is caused by the shape of the film. The cubic in-plane anisotropy \(B_{\text{cub}}\), caused by the crystal symmetry of the thin film, is responsible for the two observed easy and hard axes and shows its maximum (7 mT) at a temperature of \(T = 10\) K and its lowest value (660 mT) for \(T = 350\) K. Like the uniaxial out-of-plane anisotropy the cubic in-plane anisotropy \(B_{\text{cub}}\) decreases with increasing temperatures. We found that \(B_{\text{cub}}\) and \(B_{001}\) are thickness independent leading to the conclusion that both parameters are material properties of Co\(_2\)FeAl. The uniaxial in-plane parameter \(B_{110}\) has values of \(-3.5\ldots0\) mT and is thickness dependent, showing a complicated temperature dependence for the four Co\(_2\)FeAl films. The origin of this parameter is still under discussion. Suggested reasons causing this uniaxial in-plane anisotropy are strain [20] and a large lattice mismatch between substrate and film [22]. Comparing our anisotropy parameters with those of Co\(_2\)MnSi and Co\(_2\)MnGa, it turns out that they have the same order of magnitude.
6.2 Angle Dependent Magnetothermopower Measurements in (Ga,Mn)As and Co$_2$FeAl

Within the year of my diploma thesis a new caloritronic measurement setup was successfully assembled and ADMTP measurements were carried out in (Ga,Mn)As and Co$_2$FeAl thin films. Due to the setup we could only perform ADMTP measurements in in-plane geometry. In order to test the caloritronics setup, we decided to study the anisotropic thermopower of (Ga,Mn)As thin films first because of its high AMR, which can be seen in the resistivity anisotropy ratio $\rho_1/\rho_0 \sim 1 \ldots 3$ in (Ga,Mn)As [35]. In contrast, in Co$_2$FeAl thin films we have $\rho_1/\rho_0 \sim 0.08\%$ which leads to a small ADMTP. (Ga,Mn)As is a well known ferromagnetic semiconductor with a Curie temperature of about $100 \ldots 200$ K, depending on the doping concentration of manganese. We investigated a 30 nm thick Ga$_{0.955}$Mn$_{0.045}$As film and a 180 nm thick Ga$_{0.97}$Mn$_{0.03}$As film. A temperature gradient was applied in the [110] direction of the Hall-bars. In order to achieve good fitting results for the measured data we used terms up to the fourth order of magnetization in the simulation of the Seebeck tensor.

We could not measure the thermopower quantitatively because the Pt10k thermometers are not reliable at $T = 10$ K so that we did not know the temperature difference between the two ends of the sample. But we could show that the thermoelectric voltages are proportional to the heater power output and to the thermal gradient so that we were able to measure the Seebeck coefficient quantitatively ($V_{\text{long}} \propto \alpha_{\text{long}} = -\frac{V_{\text{long}}}{\Delta T}$). We confirmed that the Seebeck coefficient of (Ga,Mn)As is positive and depends on the angle between the magnetization and temperature gradient. The relative longitudinal thermopower of 7.5% at 10 K (magnetic field 1 T) is similar to the value published by Pu et al. [56]. In contrast, we did not see a saturation behavior for $V_{\text{therm., long}}$ although we performed AMR measurements up to 7 T.

In our ADMTP measurements the axes of the cubic anisotropy, caused by the crystal symmetry, were slightly shifted ($\sim 5^\circ$) which is not an alignment problem of the sample but already present in the free energy surface of the measurements. The shift is caused by the uniaxial $B_{110}$ anisotropy [59]. Furthermore we approved the presence of a further uniaxial anisotropy parameter $B_{100}$ in the direction of the easy cubic axis in both (Ga,Mn)As samples reported also by Pappert et al. [59]. The origin of both in-plane uniaxial parameters is still under discussion [61, 21, 60, 54], but can be influenced by annealing [21], varying the hole concentration $p$ [60] and also the temperature [21].
Chapter 6

Conclusion and Outlook

The most important issue we addressed in the ADMTP measurement is the additional parameter $S_C$ in the transverse thermopower, which is not present in the resistivity tensor model and which we discussed in detail. This is the only additional parameter in comparison to the resistivity tensor model, since the other new terms with parameters $S_A$ and $S_B$ are zero in in-plane geometry. We concluded that for the presented ip measurements of both (Ga,Mn)As samples the parameter is not (absolutely) necessary. Only out-of-plane measurements, where the influence of the $S_A$ and $S_B$ parameters might be seen, will be able to show whether the additional parameters of the phenomenological Seebeck tensor theory are needed to describe the experimental data.

In our ADMTP experiment in Co$_2$FeAl we could confirm that the thermopower is negative $\alpha < 0$, but could not resolve $\mathbf{M}$-orientation induced changes. This was expected, since $\frac{\Delta \rho}{\rho} = 0.11\%$ in Co$_2$FeAl, so that $\frac{\Delta \alpha}{\alpha} \approx 0.3\%$, which is below the resolution of the current setup. Thus improvements in the caloritronics setup are needed or other Heusler compounds with a larger magneto-Seebeck effect have to be investigated to perform ADMTP measurements successfully.

6.3 Fabrication of Co$_2$MnSi and Co$_2$FeAl targets and thin films

Another important aspect of my diploma thesis, in fact, the original planned main goal, was the fabrication of Heusler targets and Heusler thin films via pulsed laser deposition (PLD). We selected Co$_2$MnSi and Co$_2$FeAl as the PLD target material systems, because they are well known Heusler compounds and have been investigated and fabricated with PLD by various groups so that many growth parameters are available for comparison (e.g. Wang et al. [7]). We successfully fabricated Co$_2$MnSi and Co$_2$FeAl polycrystals in the induction furnace of chair E21 (TUM). Energy dispersive x-ray spectroscopy (EDX) measurements showed that the composition of the targets is close to the aimed ideal stoichiometric value of 50:25:25. For the PLD growth we concentrated our efforts on Co$_2$MnSi and optimized the growth temperature and energy density to improve the film quality.

The grown films were investigated by x-ray diffraction (XRD) measurements to analyze their structural quality, including film reflection height, mosaic spread and thicknesses. Microscope images yielded information about the surface texture of the films, especially about the size and amount of droplets. We could determine an optimum growth temper-
ature of 400 K and energy density of $3 J/cm^2$. For a higher energy density we found much more and also larger droplets ($\sim 9 \mu m$ diameter). We compared our PLD grown $Co_2MnSi$ thin films with a comparable one from the university of Bielefeld (sputtered at $T = 400 ^\circ C$ and in situ annealed for 1 hour at the growth temperature). XRD measurements revealed that the structural qualities of our PLD grown films are the same or even better as the sputtered $Co_2MnSi$ films from Bielefeld, apart from the surface roughness which is much better in the Bielefeld films, most probably due to their annealing process. The FWHM of the rocking curve is 0.86° for our film whereas in the film from Bielefeld the value is 1.49°, indicating a larger mosaic spread.

EDX measurements showed a deficit of Co in the investigated films and revealed an excess of Si. It has to be investigated thoroughly whether the growth process or the target is the reason for this issue. SQUID measurements revealed that the saturation magnetization between $M_S = 4.92 \mu B/f.u.$ and $M_S = 5.45 \mu B/f.u.$ at 50 K agrees well with the literature value of $5.07 \mu B/f.u.$[70]. Other groups found values ranging from $M_S = 4.7 \mu B/f.u.$ to $M_S = 5.1 \mu B/f.u.$, summarized by Hirohata et al. [4].

### 6.4 Outlook

For further studies it would be interesting to perform magnetotransport experiments in our $Co_2MnSi$ films and compare the results with the films from Bielefeld. The influence of the growth parameters on the magnetic anisotropy could be investigated by ADMR measurements, which could shed light on the still controversially discussed in-plane uniaxial anisotropy parameter. At the same time one could find out the quantitative value of the anisotropy parameters of $Co_2MnSi$ thin films and compare them with the determined values for $Co_2FeAl$. Also further SQUID measurements for the other fabricated films could be carried out to study the influence of the growth parameters on the magnetic properties systematically. The growth process of $Co_2MnSi$ could be further improved by annealing with regard to the surface roughness of the films, as the films from Bielefeld proved.

We only have grown one test film of $Co_2FeAl$ with the growth parameters found optimum for $Co_2MnSi$. On the surface of the $Co_2FeAl$ thin film, only a slight metallic shimmer was visible - the film was nearly transparent - which leads to the conclusion that the energy of the KrF laser was not high enough. Thus for the future growth of $Co_2FeAl$ there are different possibilities to increase the amount of material deposited onto the substrate: on the one hand we could increase the energy flux (energy per pulse) of the excimer laser or
on the other hand reduce the distance between target and substrate.
In Co$_2$FeAl thin films we have seen a sign change in the PHE parameter $\rho_7$ which could be caused by a structural change or by the stoichiometry of the sample. Future XRD measurements could be performed at low temperatures to investigate the transition region between 100\ldots150\,K for the 100\,nm thick Co$_2$FeAl film. Liquid nitrogen would be sufficient for cooling down the sample to this temperature region.

Nevertheless, the most important further investigation would be to study the new Seebeck parameters $S_A$ and $S_B$ by ADMTP measurements, which had been zero for the performed $ip$ measurements. This implies the construction of a new sample holder allowing us to conduct out-of-plane experiments or even better define an arbitrary rotation axis where both $S_A$ and $S_B$ are non-zero. Our calculation of $S_B$ shows that the parameter holds most promise to be detectable in the experiments in comparison to $S_A$ and $S_B$. If these future measurements show the need of the new Seebeck coefficients, this would prove the correct adaption of the resistivity model for the Seebeck tensor experimentally, which would be a great success in the caloritronics field of research.

Another improvement would be to use new temperature sensors which can detect temperatures below 73\,K. Another option would be to use thermocouples to precisely detect the temperature on the film surface and to measure the thermoelectric voltage simultaneously to the temperature gradient.

In conclusion, the investigation of Heusler and (Ga,Mn)As thin films by ADMR and ADMTP measurements, offers a very interesting research field that yields many open questions, in particular with respect to the magnetic anisotropy, and is essential for future spintronics applications.
Appendix A

A.1 Seebeck Tensor Calculations

Here we present all 33 parameters needed to describe the Seebeck tensor in tetragonal crystal symmetry:

\[
\begin{align*}
A_1 &= s_{22} + s_{2211} + s_{221111} \\
A_2 &= s_{33} + s_{3322} + s_{333322} \\
B_1 &= s_{213} + 3s_{21311} \\
B_2 &= s_{323} + 3s_{32322} \\
B_3 &= s_{231} + 3s_{21322} \\
B_4 &= s_{231} + 3s_{23221} \\
C_1 &= s_{2222} - s_{2211} + 6s_{222111} - 2s_{221111} \\
C_2 &= s_{3333} - s_{3322} + 6s_{333322} - 2s_{332222} \\
C_3 &= 2s_{2121} + 4s_{212111} \\
C_4 &= 2s_{2322} + 4s_{232222} \\
C_5 &= 2s_{2121} + 4s_{212221} \\
C_6 &= 2s_{2332} + 4s_{233222} \\
C_7 &= s_{2333} - s_{2211} - 6s_{222111} + 6s_{223322} \\
D_1 &= s_{21333} - 3s_{213111} \\
D_2 &= s_{21311} - 3s_{21322} \\
D_3 &= s_{21333} - 3s_{21332} \\
D_4 &= s_{21311} - 3s_{23221} \\
D_5 &= 3s_{21322} - 3s_{213111} \\
D_6 &= 3s_{32331} - 3s_{23321} \\
D_7 &= 3s_{23331} - 3s_{23321} \\
D_8 &= 6s_{22321} \\
E_1 &= s_{2222} - 6s_{222211} + s_{221111} \\
E_2 &= s_{333333} - 6s_{333322} + s_{332222} \\
E_3 &= 6s_{223311} + 6s_{222211} - 6s_{233322} + 2s_{221111} \\
E_4 &= 6s_{332211} - 2s_{332222} \\
E_5 &= 12s_{213321} - 4s_{212111} \\
E_6 &= 12s_{332211} - 4s_{333322} \\
E_7 &= 12s_{213321} - 4s_{212221} \\
E_8 &= 12s_{233211} - 4s_{233222} \\
E_9 &= s_{233333} + 6s_{222211} - 6s_{223322} + 3s_{221111} \\
E_{10} &= 4s_{212221} - 4s_{212111} \\
E_{11} &= 4s_{323332} - 4s_{323222} \\
E_{12} &= 4s_{233332} - 4s_{233222}
\end{align*}
\]

For the longitudinal and transverse Seebeck coefficients the following parameters were
used:

\[ S_0 = s_{22} + s_{2121} + \frac{s_{2211}}{2} + \frac{s_{2222}}{2} + s_{212111} + s_{212221} + \frac{s_{221111}}{4} + \frac{3s_{222211}}{2} + \frac{s_{222222}}{4} \]

\[ S_1 = 2s_{2121} + 2s_{212111} + 2s_{212221} + s_{221111} - 6s_{213321} + s_{222222} \]

\[ S_2 = s_{2121} + s_{2233} - \frac{s_{2211}}{2} - \frac{s_{2222}}{2} + 2s_{212111} + 2s_{212221} - 6s_{213321} - \frac{s_{221111}}{2} - \frac{s_{222222}}{2} - 3s_{222211} + 3s_{223311} + 3s_{223322} \]

\[ S_3 = -s_{221111} + 6s_{222211} - s_{222222} \]

\[ S_4 = -s_{212111} - s_{212221} + s_{223333} + 6s_{213321} + \frac{3s_{222211}}{2} + \frac{s_{221111}}{4} + \frac{s_{222222}}{4} - 3s_{223311} - 3s_{223322} \]

\[ S_5 = -2s_{212111} - 2s_{212221} + 6s_{213321} - s_{221111} + 6s_{222211} - s_{222222} \]

\[ S_A = -3s_{21311} + 3s_{21322} \]

\[ S_6 = s_{213} + \frac{3s_{21311}}{2} + \frac{3s_{21322}}{2} - 3s_{22321} \]

\[ S_7 = -s_{2211} + s_{2222} + 2s_{212111} - 2s_{212221} - s_{221111} + s_{222222} \]

\[ S_8 = -\frac{3s_{21311}}{2} - \frac{3s_{21322}}{2} + s_{21333} + 3s_{22321} \]

\[ S_9 = -2s_{212111} + 2s_{212221} + s_{221111} - s_{222222} - 6s_{223311} + 6s_{223322} \]

\[ S_B = 6s_{22321} \]

\[ S_C = -4s_{212111} + 4s_{212221} \]

Formulae derived from the identity \( m_x^2 + m_y^2 + m_z^2 = 1 \) used for simplifying the tensor equation:

\[
(m_x^2 m_z^2 + m_y^2 m_z^2) = m_z^4 - m_z^2 \quad (A.1)
\]

\[
(m_x^4 + m_y^4) = 1 - 2m_x^2 + m_x^4 - 2m_x^2 m_y^2 \quad (A.2)
\]

\[
m_y^4 = 1 - 2m_y^2 + m_y^4 - 2m_x^2 m_y^2 - m_x^4 \quad (A.3)
\]

\[
m_x m_y = \frac{1}{2}((m_x + m_y)^2 - 1 + m_x^2) \quad (A.4)
\]

\[
m_x^2 m_y^2 = \frac{1}{4}((m_x + m_y)^4 + 1 + m_y^4 + 2(m_x + m_y)^2 m_x^2 - 2(m_x + m_y)^2 - 2m_x^2) \quad (A.5)
\]
A.2 EDX measurements

Additional EDX-measurement of the larger sides of the Heusler targets.

<table>
<thead>
<tr>
<th></th>
<th>1. pos.</th>
<th>2. pos.</th>
<th>3. pos.</th>
<th>4. pos.</th>
<th>5. pos.</th>
<th>6. pos.</th>
<th>7. pos.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>51.78%</td>
<td>51.55%</td>
<td>51.63%</td>
<td>51.36%</td>
<td>51.12%</td>
<td>50.88%</td>
<td>51.72%</td>
</tr>
<tr>
<td>Mn</td>
<td>25.35%</td>
<td>24.97%</td>
<td>24.93%</td>
<td>24.90%</td>
<td>24.95%</td>
<td>24.83%</td>
<td>24.99%</td>
</tr>
<tr>
<td>Si</td>
<td>22.87%</td>
<td>23.48%</td>
<td>23.44%</td>
<td>23.74%</td>
<td>23.94%</td>
<td>24.09%</td>
<td>23.29%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>1. pos.</th>
<th>2. pos.</th>
<th>3. pos.</th>
<th>4. pos.</th>
<th>5. pos.</th>
<th>6. pos.</th>
<th>7. pos.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>52.57%</td>
<td>53.18%</td>
<td>52.13%</td>
<td>52.18%</td>
<td>52.41%</td>
<td>52.26%</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>26.78%</td>
<td>28.03%</td>
<td>26.63%</td>
<td>27.60%</td>
<td>27.29%</td>
<td>26.82%</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>20.65%</td>
<td>18.79%</td>
<td>21.24%</td>
<td>20.22%</td>
<td>20.29%</td>
<td>20.92%</td>
<td>-</td>
</tr>
</tbody>
</table>

Table A.1: Calculated percentage of the elements found at the 6...7 different positions (pos.) on the targets. An ideal full-Heusler has the element composition ratio of 50:25:25. The first measurement area is at one edge of the target, the next closer to the center and so on. The last measurement is carried out at the opposite edge of the target. Here the analysis was done for the larger sides of both targets.
Bibliography


[64] A. Bauer, Quantenphasenübergänge und Skyrmion-Gitter in Mn_{1-x}Fe_{x}Si und Mn_{1-x}Co_{x}Si, Diploma thesis, TU Munich (2009).


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