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EuS based thin film layered systems

Magnetoresistance and coupling phenomena

Proefschrift

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The cartoon on the cover is an impression of spin filtering by a spin-dependent tunnel barrier.
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Chapter 1

Introduction

This thesis treats various aspects of an attempt to achieve spin filtering with EuS. Since no common and unique definition of spin filtering exists, the spin filtering effect will first be introduced and a definition will be included. In parallel, the aim of the research will be explained.

An interesting starting point for an introduction to the spin filter effect is to consider it as the next-generation source of a spin polarized current. A spin-polarized current is a current that consists of unequal amounts of spin-up and spin-down electrons. In principle, the most straightforward source of a spin-polarized current is an ordinary (metallic) ferromagnet. The principle of spin polarization by a normal metallic ferromagnet is schematically shown in figure 1.1a. Initially, in the nonmagnetic metal the current is unpolarized. While flowing through the ferromagnet the current becomes spin polarized, due to different mean free paths for electrons of both spin orientations and due to different concentrations of electrons available for transport, as indicated by the unequal amount of spin-up and spin-down electrons in the cartoon. The spin polarization of the current persists at least to some extend into the second nonmagnetic metal. A second configuration for spin polarizing a current is a ferromagnet - tunnel barrier combination, as depicted in figure 1.1b. In this case the current is governed by the tunneling process and, as a result, the spin-polarizing effect originates from the polarization in the ferromagnet at the interface with the tunnel barrier, in which the polarization of the ferromagnet refers to the relative amount of spin-up and spin-down electrons that are available in the ferromagnet for tunneling through the barrier. A third method of spin polarizing a current would be not to tunnel from a ferromagnet through a nonmagnetic tunnel barrier, but to make the tunnel barrier itself spin dependent. This is schematically shown in figure 1.1c. In this thesis such a spin-dependent tunnel barrier is called a spin filter. In the next chapter it will be explained that a magnetic tunnel barrier, which can be either a magnetic, intrinsic semiconductor or a magnetic insulator, will have different transmission probabilities for spin-up and spin-down electrons.
An important difference between the three sources of spin polarization relates to the maximum current polarization that can be achieved. If the spin polarization is introduced from a metallic ferromagnet (figure 1.1a and b), the current polarization can never exceed the polarization of the ferromagnet (resistance or tunneling spin polarization, respectively). A spin filter on the other hand will become more and more efficient as it is made thicker, which will be explained in detail in chapter 2, resulting in a current spin polarization up to 100%. A special limiting case is a so-called half metal. This is a material that shows metallic behavior for electrons of one spin orientation, and provides a tunnel barrier for electrons of the other spin orientation. Since the polarization of the current occurs as a result of the finite tunneling probability of electrons of one spin orientation, a half metal can be considered as a spin filter. Alternatively, as the transport of electrons of the other spin orientation is metallic, a half metal can also be regarded as a ferromagnetic metal with a polarization of 100%.

To summarize, a spin filter is in this thesis by definition a spin-selective tunnel barrier. In chapter 2 it will be demonstrated that a magnetic (intrinsic) semiconductor or insulator can provide such a tunnel barrier. A regular metallic ferromagnet is not considered a spin filter here. It is not a tunnel barrier, and, instead of really filtering the spins, it more or less replaces the spin orientation of the passing electrons with that of its own electrons. The limiting case is a half metal, that behaves as a tunnel barrier for electrons of one spin orientation, while it shows metallic behavior for electrons of the other spin orientation.

Any two of the above mentioned sources of spin-polarized currents, placed in series in a polarizer-analyzer fashion, lead to various magnetoresistance effects. Two ordinary ferromagnets give rise to the so-called Giant Magnetoresistance (GMR) effect, discovered independently by Baibich et al. and Binasch et al. in 1988 [1, 2], if they are placed close to each other so that spin flip is of minor importance. The combination of a tunnel barrier with two magnetic electrodes results in the Tunnel Magnetoresistance (TMR) effect, that was discovered by Moodera et al. in 1995 [3]. Recently, we proposed the use of two spin filters in series to create a magnetoresistance effect [4]. Also the combination of a magnetic electrode with a spin filter, which is a combination of figure 1.1b and c, should lead to a magnetoresistance effect. This effect was indeed observed by LeClair et al. [5], who proposed the name Spin Filter Magnetoresistance (SFIM). Systems based on one or more spin filter layers will be the topic of this thesis.

A spin filter is also expected to give rise to important applications in the field of semiconductor spintronics. Semiconductor spintronics is an extension of normal semiconductor electronics, in which also the electron spin is used. Its applications range from fast non-volatile memories, to field sensors and electronic circuits that can be modified using magnetic fields. Many reviews on various levels exist already discussing the advantages of spintronics as compared to ordinary electronics [6–9]. Fert et al. [8] divide the new possibilities resulting from
Chapter 1. Introduction

Figure 1.1: Spin polarization of an electron current flowing from left to right by (a) a metallic ferromagnet (FM), (b) a combination of a metallic ferromagnet and a nonmagnetic tunnel barrier (TB), and (c) a spin filter (SF). Nonmagnetic metals are denoted by NM. The ratio of drawn spin-up and spin-down electrons denotes the relative contribution of the respective spin channels to the current.

A spin-electronic operation that combines optical, electrical and magnetic properties of semiconductors can, somewhat arbitrarily, be considered as a three-step process: injection of spins into a semiconductor, the actual operation on the spin, and the detection of the resulting spin. Achieving a good efficiency of electrical injection and detection is still an important challenge. For reasons that will be explained in the next chapter (the so-called impedance mismatch) direct injection of a spin-polarized current from a metallic ferromagnet only leads to low current polarizations. The two alternative sources of a spin-polarized current as mentioned above, a ferromagnetic electrode - tunnel barrier combination and a spin filter, do not suffer from this problem. It is thus possible to overcome this obstacle by inserting a tunneling barrier between the metal and semiconductor [10, 11]. Alternatively, a spin filter can be used for electrical injection [5] of a
spin polarized current.

As mentioned before, both ferromagnetic semiconductors and insulators can in principle be used as a spin filter. For the research that is described in this thesis the well-studied magnetic semiconductor europium sulfide (EuS) was selected as a model system. Ferromagnetism in EuS was discovered in 1962 by various groups [12–14], shortly after the discovery of ferromagnetism in europium oxide (EuO) at low temperatures by Matthias et al. [15], see figure 1.2. Compared to each other, EuO has a higher Curie temperature (77 K) than EuS (16.8 K), but EuS has the advantage of a better chemical stability than EuO. For a study of the principles behind spin filtering foremost a model system is needed. Therefore, for our material choice for spin spin filtering the better chemical stability of EuS was considered as more important than its lower Curie temperature.

The physical properties of EuS are well-documented in a series of review papers [16–18]. EuS has a rock-salt structure with a lattice parameter of 5.97 Å and the bottom of its conduction band is 1.65 eV above the Fermi level. EuS is commonly used as an “ideal” example of a Heisenberg ferromagnet, with exchange coupled, localized 4f electrons. Recently, LeClair et al. used EuS as a spin filter in a magnetoresistance device by combining it with a single (metallic) magnetic electrode. A magnetoresistance ratio of 130% at a temperature of 2 K was obtained [5], indicating that spin filtering using EuS must indeed be possible. Moreover, LeClair et al. showed that EuS layers of sufficient quality can in principle be grown by sputtering, a technique that allows for a rapid production of samples.

As to the application of spin filters, three main issues in the further development can be discerned: the efficiency of the spin filter, magnetic controllability, and its operating conditions.

The issue of spin filter efficiency includes improvement of the efficiency of the spin filter itself as well as a more efficient incorporation of the spin filter in a device. The efficiency can be changed by variation of materials, or, alternatively, by improving the growth and structure of a device containing a spin filter.

If spin-filter layers are to be used in electronic applications, magnetic controllability is necessary, in other words it has to be possible to tune their switching fields. Generally there are two ways of modifying the switching field of a ferromagnet: exchange biasing by an antiferromagnet or making use of interlayer coupling. In the former case the ferromagnet is brought in contact with an antiferromagnet such that the two layers become exchange coupled [19, 20], as is successfully applied for metallic structures [21]. The latter solution takes advantage of the interlayer coupling between two ferromagnetic layers. Interlayer coupling is the magnetic interaction between two magnetic layers that are separated by a thin nonmagnetic spacer layer. If the interaction is antiferromagnetic the two layers prefer an antiparallel alignment. As a result, the switching fields of the ferromagnets are shifted with respect to those of single ferromagnetic lay-
Figure 1.2: The inverse of the magnetic susceptibility as a function of temperature for the Eu chalcogenides EuO, EuS, EuSe and EuTe. It can be seen that at the Curie temperature of EuS, EuSe and EuO the magnetic (volume) susceptibility diverges, a sign of spontaneous magnetization. The data are taken from the original papers by Matthias et al. [15], who first reported ferromagnetism in EuO, and by Van Houten [14], who found ferromagnetism in EuS and EuSe and antiferromagnetism in EuTe. The data were measured at various fields of 637 kA/m for EuO, 51-145 kA/m for EuS, 145-362 kAm/m for EuSe, and 245 kA/m for EuTe.

ers. However, the study of the magnetic interlayer coupling in all-semiconductor structures is not only of technological relevance [22], but is also of fundamental interest, as no theory is yet available on the interlayer coupling in semiconductor structures.

With respect to the operational conditions of a spin filter, one of the most important limitations to their application for electronics is their operating temperature. Currently no room temperature ferromagnetic semiconductor, that would qualify as a spin filter, is available, although the development of magnetic semiconductors at room temperature is promising, and much effort is put into it [22]. Some insulators are magnetic at room temperature, but their growth as a thin spin filtering tunnel barrier has not yet been demonstrated at room temperature [23–26]. Thus the quest is to obtain a ferromagnetic semiconductor or insulator that can be reliably grown as a spin filter tunnel barrier and that operates at room temperature. It is also desired that the spin filter is compatible with the current silicon processing technology. A spin filter that is not compatible has a smaller chance to be used by current industry, as it would be more expensive
to manufacture.

In this thesis all of the issues mentioned above will be addressed to a certain extend. In chapters 4 and 5 the efficiency of devices based on a spin filter is treated. Chapter 4 reports on an optimization study of EuS as a specific spin filter tunnel barrier and discusses magnetic interaction between a spin filter and the electrodes. Chapter 5 describes the results of calculations on the magnetoresistance that could be achieved with two spin filters in series. The magnetic controllability is discussed in chapter 6, where the physics behind interlayer coupling in semiconductor multilayers is investigated, which in principle allows for modification of the switching field of a spin filter. Finally, the topic of increasing the operating temperature is briefly touched in chapter 7, in which it is shown that the europium chalcogenide EuTe (also shown in figure 1.2), that is normally an antiferromagnet, can become ferromagnetically ordered, although still at low temperatures, by adding charge carriers via Gd doping.
Chapter 2

Basics of spin-dependent transport, interlayer coupling, and magnetic semiconductors

This chapter contains theory that is required for understanding the basic physics behind the results described in this thesis. The chapter covers three important subjects: spin-dependent electron transport, magnetic semiconductors, and interlayer coupling. As to the electron transport, both diffusive and tunneling transport are discussed. For the diffusive transport, first a simple picture of carrier transport of unpolarized electrons will be presented, which will be extended to the spin-polarized case afterwards, based on a so-called two-current (spin up and down) model. The second section discusses magnetic semiconductors. For EuS it is explained why a magnetic semiconductor layer can act as a spin-selective tunnel barrier. Finally, a section is devoted to an introduction to the field of magnetic interlayer coupling, the tendency of two spatially separated magnetic layers to assume correlated magnetization directions, with a focus on the coupling in semiconductor systems.

2.1 Spin dependent electron transport

In this thesis the transport of electrons in devices based on semiconductor layers is described by either of the two following models. (I) The transport through an intrinsic semiconductor or insulator sandwiched between metallic contacts, like is the case for thin EuS layers, is described by electron tunneling. (II) Transport in metals and heavily degenerated semiconductors is written in terms of drift and diffusion. In this section these two types of electron transport will be introduced.
Drift-diffusion transport

For the diffusive transport the so-called drift-diffusion model is used. In this model the density and transport properties of a certain population of charge carriers are simply described by diffusion and drift due to an effective electric field. An extensive discussion is given by Smith [27]. Here the description of electron transport in terms of conductivities will be related to diffusion for use in chapter 5.

The situation of a 1-dimensional electron distribution is considered. The situation is practically accomplished in materials with a partially filled conduction band, like metals, but also a heavily degenerate semiconductor like PbS, that will be used in chapter 5, can be described in this way. Since diffusion is driven by the gradient in carrier density (Fick’s law) the resulting current density \( J_{\text{diff}} \) is:

\[
J_{\text{diff}} = eD\frac{\partial n}{\partial x}
\]  

(2.1)

where \( e \) is the electron charge, \( \frac{\partial n}{\partial x} \) is the gradient of the electron density, and \( D \) is the diffusion constant. As a result of diffusive transport an electric field can arise, that will oppose the diffusion current. A drift current \( J_{\text{drift}} \) is generally written as a function of the electric field within the well-known Ohm’s law:

\[
J_{\text{drift}} = \sigma E = ne\mu E
\]  

(2.2)

where \( E \) is the (1-dimensional) electric field. In thermodynamic equilibrium both components to the current in the drift-diffusion equation cancel and the net current \( J \) equals zero:

\[
J = ne\mu E + eD\frac{\partial n}{\partial x} = 0.
\]  

(2.3)

The next step would be evaluation of the derivative \( \frac{\partial n}{\partial x} \). For the evaluation of this expression, a clear picture of the energy levels involved is desired. Figure 2.1 shows the electron density as a function of energy for a Fermi-Dirac distribution. Under the assumption that any variation in the electron density is purely determined by the electrostatic effect of the electric field on the energy level of the conduction band as a whole, the derivative can be split into \( \frac{\partial n}{\partial x} = \frac{\partial n}{\partial E_c} \frac{\partial E_c}{\partial x} \), with \( E_c \) representing the energy level of the bottom of the conduction band. The last part of this expression can be written as:

\[
\frac{\partial E_c}{\partial x} = -\frac{\partial eV}{\partial x} = eE
\]  

(2.4)

where \( V \) is the potential associated with the electric field. For a mathematical description of \( \frac{\partial n}{\partial E_c} \), first the electron density is written as the integral of energy over the whole conduction band:

\[
n = \int_{E_c}^{\infty} N(E - E_c) f_0(E) dE = \int_{0}^{\infty} N(E_1) f_0(E_c + E_1) dE_1,
\]  

(2.5)
in which \( E_1 \) is the electron’s energy measured from the bottom of the conduction band and \( f_0 \) is the Fermi-Dirac distribution function. Next the derivative with respect to \( E_c \) has to be taken:

\[
\frac{\partial n}{\partial E_c} = \frac{\partial}{\partial E_c} \int_0^\infty N(E_1) f_0(E_c+E_1) dE_1 = \int_0^\infty N(E_1) \frac{\partial}{\partial E_c} \left( f_0(E_c+E_1) \right) dE_1. \tag{2.6}
\]

A visual representation of the above reasoning is given in figure 2.1, in which a shift in energy of the bottom of the band by \( dE_c \) leads to a decrease in carrier density indicated by the shaded area. The derivative of the Fermi-Dirac function transforms into a delta function at the Fermi energy for temperatures approaching absolute zero. Equation 2.6 reduces then to

\[
\frac{\partial n}{\partial E_c} = -N(E_F). \tag{2.7}
\]

Substitution of \( \frac{\partial n}{\partial x} \) into 2.3 gives the so-called Einstein relation, that links the drift-diffusion description to the conductivity, for systems with a partially filled conduction band:

\[
\sigma = ne\mu = N(E_F)e^2D. \tag{2.8}
\]

In words, the conductivity depends on the amount of electrons that are available for transport, which is proportional to \( N(E_F) \), and on the diffusion constant for electrons.

For non-degenerate semiconductors the Einstein relation can be written in a somewhat different form. In this case Boltzmann statistics apply and the carrier density is proportional to \( e^{eV/k_BT} \), where \( k_B \) is Boltzmann’s constant. Substituting this into the drift-diffusion equation (equation 2.3) gives the Einstein relation
for non-degenerate semiconductors:

\[ D = \frac{k_B T}{e \mu}. \tag{2.9} \]

This is the original equation developed by Albert Einstein in his 1905 paper to describe the Brownian motion \[28\]. However, since PbS is always heavily n-doped and the Fermi level is at the bottom of the conduction band \[29\], for the transport through PbS equation 2.8 still has to be used (see chapter 5).

In general, the Einstein equation relates the conductivity of a material to the diffusion constant. Alternatively, the validity of the Einstein relation corresponds to the equality of the well-known Ohm’s law and Fick’s law (equation 2.1), describing diffusion driven transport.

Turning now to spin-dependent electron transport, two general approaches can be applied in this case. The first, more rigorous method, is to calculate the so-called chemical potential for both spin species. Valet and Fert \[30\] showed that the Boltzman transport equation model reduces to macroscopic transport equations when the spin flip length is much longer than the mean free path of the electrons. From solving the diffusion equation they obtain both the current and the chemical potential throughout a complete system. This approach has been applied to many layered structures combining ferromagnetic metals, nonmagnetic metals and semiconductors, in order to calculate their resistance and magnetoresistance \[11, 31, 32\].

If the spin flip time is longer than the electron scatter time, electrons of spin-up and spin-down orientation can be considered as two separate species. Spin flip is then taken into account as the creation of electrons of one spin orientation combined with a parallel annihilation of electrons of the other orientation. Such an approach is referred to as a two-current model, first introduced by Mott \[33, 34\] to describe the conductivity in transition metals. In a two-current model the total current is written as the sum of two parallel currents of electrons of each spin orientation. Two-current models have been applied successfully in the research of the giant magnetoresistance effect \[35\]. Here, the so-called impedance mismatch problem, probably the most fundamental obstacle for spin-injection into semiconductors, will be explained using a simple two-current resistor model.

Figure 2.2 shows the situation of a ferromagnet in contact with a nonmagnetic material as described within the framework of a two-current resistor model. The current \( I \), flowing from left to right, is split in spin up and spin down contributions. For simplicity the two current channels are taken completely insulated from each other, in other words spin flip processes inside the structure are not considered. The resistance of the magnetic material in the structure is taken to be spin dependent. For the nonmagnetic layer \( R_{N,\uparrow} \) and \( R_{N,\downarrow} \) are equal to each other (having a value of \( 2R_N \)), where the factor of 2 originates from the fact that addition of the two resistances in parallel results in a net resistance of only half
Chapter 2. Basics

their value. The resistance $R$ of the complete scheme in figure 2.2 is given by

$$R = \frac{(R_{F,\uparrow} + 2R_N)(R_{F,\downarrow} + 2R_N)}{R_{F,\uparrow} + R_{F,\downarrow} + 4R_N}.$$  \hspace{1cm} (2.10)

The resistance mismatch problem occurs when the resistance of the nonmagnetic material is much higher than that of the ferromagnet. This is usually the case if the ferromagnet is a metal (like Fe, Co, Ni) while the nonmagnetic material is a semiconductor (e.g. GaAs or Si). Then the total resistance (Equation 2.10) is almost completely determined by the resistance of the nonmagnetic semiconductor $R_N$. Moreover, the resistances of the two current branches are almost equal, and as a result the relative current difference is small:

$$\frac{I_{\uparrow} - I_{\downarrow}}{I_{\uparrow} + I_{\downarrow}} = \frac{R_{F,\uparrow} - R_{F,\downarrow}}{R_{F,\downarrow} + R_{F,\uparrow} + 4R_N}.$$  \hspace{1cm} (2.11)

Thus it can be concluded that efficient injection of a spin-polarized electron current from a metallic ferromagnet into a semiconductor via diffusive transport is hampered by the large difference in their resistance [36]. This so-called impedance mismatch was first described by Schmidt et al. [37], but then based on solving the diffusion equation for the chemical potential throughout the system. It is an important problem in the field of spin injection (from metals) into semiconductors. Since a tunnel contact allows for a higher spin-dependent resistance than an Ohmic contact, efficient injection of a spin-polarized current is nowadays achieved mostly through tunnel contacts instead of Ohmic contacts, as will be the case in this thesis.

\begin{align*}
\text{Figure 2.2: Resistor scheme of a current through ferromagnetic (F) and a nonmagnetic material (N) within a two-current resistor model, in which the current flowing from left to right is split in a spin up (upper channel) and a spin down (lower channel) component. The resistance of the ferromagnet for spin up and down electrons is } R_{F,\uparrow} \text{ and } R_{F,\downarrow}, \text{ respectively; the resistance of the nonmagnetic material is } R_{N,\uparrow} \text{ and } R_{N,\downarrow}.\end{align*}
Tunneling transport

Next to diffusion, tunneling is the second type of transport that will be discussed in this thesis. Tunneling is a quantum mechanical transport mechanism that describes transport from one side of a potential barrier to the other, that is not allowed within classical mechanics. The transmission and reflection of a free electron at a finite potential barrier is a typical textbook example in quantum mechanics. The transmission probability $T$ of an electron through a finite barrier is given by [38]

$$T = e^{-2 \int \sqrt{2m/\hbar^2}|U(x)-E|dx}, \quad (2.12)$$

in which $m$ denotes the electron’s effective mass, $\hbar$ is Dirac’s constant, and $U(x)-E$ is the barrier height at position $x$ for an electron of energy $E$. The integral is taken over the barrier region. For tunneling from one state to another, as is the case when an electron tunnels from a metallic electrode through a semiconductor or an insulator, Fermi’s Golden Rule can be applied: the electron transition rate is proportional to the amount of filled initial states multiplied by the amount of available final states and by a so-called squared matrix element [38]. In the specific case of a tunnel junction the tunnel current for electrons at a certain energy level is thus proportional to the amount of occupied states at one side of the barrier, multiplied by the amount of empty states of the same energy at the other side. The matrix element describes the tunneling process itself, including the properties of the barrier and interface effects, etc. [39]. When a finite bias $V$ is applied, the current through a tunnel junction can thus be written as

$$I(V) = \int_{-\infty}^{+\infty} \rho_l(E)\rho_r(E+eV)|M|^2f(E)[1-f(E+eV)]dE, \quad (2.13)$$

in which $\rho_l(E)f(E)$ is the amount of filled states at the left contact (left side density of states times the Fermi-Dirac filling function) and $\rho_r(E+eV)[1-f(E+eV)]$ is the amount of empty states at the right contact (right side density of states times “1 minus the Fermi-Dirac function”). The tunnel current is the integral of the number of electrons that tunnel from one side of the barrier to the other at all energies $E$. For a more precise description, conservation of the transverse wavevector $\vec{k}_{\text{trans}}$ in the tunneling process could be implemented [40]. However, for systems with non-epitaxial electrodes and amorphous barriers, conservation rules for the transverse wavevector are broken, making an analysis based on $\vec{k}_{\text{trans}}$ conservation invalid [41]. Moreover, as this thesis will be mainly focussing on the qualitative demonstration of spin filtering magnetoresistance effects, taking into account $\vec{k}$-conservation is not necessary and, therefore, omitted.

For the evaluation of the matrix element often the Wentzel-Kramers-Brillouin (WKB) approximation technique is applied. In the WKB approximation the potential in the system is treated as a juxtaposition of square barriers, and the total tunnel probability is taken as the product of the tunnel probabilities through
the individual square barriers. This is only allowed if the potential varies slowly with respect to the extinction length of the wavefunction in the barrier [38]. Simmons [42] used the WKB approximation to derive an expression for the tunnel current density through a junction with two equal electrodes. Brinkman [43, 44] extended the result to tunnel junctions consisting of electrodes that are not the same, leading to a “triangular” barrier:

\[ I(V) = G_0 \left( V - \frac{\sqrt{2m_e d \Delta \phi}}{24h} \frac{e^2}{\phi^{3/2}} V^2 + \frac{me^2 d^2}{12h \phi} V^3 \right) \] (2.14)

with

\[ G_0 = \frac{e^2 \sqrt{2m_0} \phi^{1/2}}{4\pi^2 h^2 d} e^{-\frac{2\sqrt{2m_0} \phi^{1/2}}{9}}, \] (2.15)

where \( \phi \) is the average barrier height that has an asymmetry \( \Delta \phi \), which is the difference in barrier height at both sides of the barrier. \( G_0 \) is the conductance of the junction if no bias voltage is applied. The barrier thickness is denoted by \( d \).

If both electrodes are magnetic a magnetoresistance is expected. This is known as the tunnel magnetoresistance effect, first demonstrated in 1995 by Moodera et al. [3]. In order to quantify this magnetoresistance the tunnel current is evaluated for each spin orientation separately. The tunnel current for electrons of both spin orientations obeys equation 2.13, and it thus depends on the spin-dependent density of states at both sides of the barrier. From a calculation of the total (spin-up and spin-down) tunnel current for the magnetic electrodes both in parallel and in antiparallel alignment, the magnetoresistance ratio MR can be derived. The MR is commonly defined as the difference in resistance between the antiparallel (\( R_{\text{AP}} \)) and the parallel (\( R_P \)) magnetic alignment of the electrodes relative to the resistance in the parallel alignment. The MR is usually not given in terms of the spin-dependent density of states at the Fermi level, but instead it is written as a function of the polarization of the left and right electrode, \( P_L \) and \( P_R \), respectively. The polarization \( P \) is defined as the relative difference in density of states at the Fermi level for majority (\( \rho_{\text{maj}} \)) and minority (\( \rho_{\text{min}} \)) electrons:

\[ P = \frac{\rho_{\text{maj}} - \rho_{\text{min}}}{\rho_{\text{maj}} + \rho_{\text{min}}} \] (2.16)

The magnetoresistance ratio of a magnetic tunnel junction, written in terms of the polarization of the electrodes, was first derived by Jullière [45] and is given by

\[ \text{MR} = \frac{R_{\text{AP}} - R_P}{R_P} = \frac{2P_L P_R}{1 - P_L P_R}. \] (2.17)

This so-called Jullière equation describes how the magnetoresistance of a tunnel junction increases as the polarization of the electrodes increase from 0 (unpolarized) to 1 (completely polarized).

In chapter 4 systems based on a magnetic electrode combined with a magnetic tunnel barrier will be discussed. The “Jullière” formula for such systems will also be derived and compared to equation 2.17.
2.2 The ferromagnetic semiconductor EuS as a spin filter

As mentioned before, the main topic of this thesis is spin filtering, which is defined here as generating a spin-polarized current by tunneling through a spin-dependent potential barrier. Tunneling transport was already described from basic quantum mechanics in the previous section, and the tunnel barrier transmission was given in equation 2.12. For a spin-selective barrier, equation 2.12 can be used to describe transport of electrons of each spin orientation separately by substitution of a different barrier height for electrons of each spin orientation. The question now is how such a spin-dependent tunnel barrier can be realized. In this section it is shown that a magnetic (intrinsic) semiconductor could, in principle, provide spin filtering.¹

Since this thesis deals with EuS as the spin filtering material, the formation of a spin-dependent tunnel barrier in semiconductors will be discussed on the basis of EuS. However, the reasoning can also be applied to other semiconductors with low carrier concentrations. Eu has atomic number 63, and an electron configuration of Xe 6s² 4f⁷. In EuS the Eu atom is ionized and it gives up its two 6s electrons. The remaining half-filled 4f shell is completely spin polarized according to Hund’s rules, producing a large magnetic moment on the Eu²⁺ ions. The band structure of EuS can be thought of as a combination of the orbitals of the Eu²⁺ and S²⁻ ions, although the 4f states are strongly localized and are hardly affected by mixing with the S²⁻ orbitals. Rigorous calculations lead to a band structure that is indeed in agreement with the above considerations [46]. Güntherodt et al. [47] measured the maxima in the absorption spectrum of EuS and related this to interband electron transitions. From their measurements they derived the electron density of states of EuS, that is presented in figure 2.3.

Below the Curie temperature the (4f) magnetic moments of all Eu²⁺ ions align. As a result all bands in EuS experience an exchange field from the spin polarized 4f electrons, and they become exchange split. In particular, the 5d conduction band is exchange split by an amount ∆, as indicated in figure 2.3, which results in a spin-split band edge. This spin splitting was first observed in optical studies in which the observed redshift of the absorption edge was ascribed to the splitting of bands [17]. Later experiments exploiting this exchange splitting will be discussed in chapter 4. Because of this exchange splitting the barrier height experienced in a tunneling process is spin dependent. If the magnetization of the EuS is such that the exchange splitting lowers the barrier height for spin-up and raises it for spin-down electrons, their respective transmission probabilities through a barrier

¹A problem might occur for heavily doped semiconductors such as GaMnAs, where the main transport mechanism is usually drift of holes instead of tunneling.
Figure 2.3: Impression of the energy level scheme of EuS extracted from literature [17, 18, 47]. The completely filled 4f\textsuperscript{7} band is one half of the total 4f density of states and contains only electrons of one spin orientation. The other half of the density of states is unoccupied and is located at a much higher energy. As a result, upon the magnetic alignment of the 4f electrons from different atoms below the Curie temperature of 16.8 K the other bands become exchange split with an exchange splitting $\Delta$, as indicated for the 5d conduction band in the right part of the figure.

of a constant height $\varphi \pm \Delta$ and a thickness $d$ are given by:

\[
T_\uparrow \approx e^{-2d\sqrt{\frac{\varphi}{\pi^2}} \varphi - 1/2\Delta} \\
T_\downarrow \approx e^{-2d\sqrt{\frac{\varphi}{\pi^2}} \varphi + 1/2\Delta}.
\]

For a magnetic semiconductor like EuS the tunneling probability is thus spin dependent, and EuS is a true spin filter. More general, for any material that is either semiconducting or insulating no states are available at the Fermi energy and a finite barrier height exists. If such a material is also ferromagnetic and its bands become exchange split, its barrier height for electron tunneling becomes spin dependent. A magnetic semiconductor is thus a suitable material for spin filtering. Recently, indeed spin filtering was observed with other magnetic semiconductors and insulators as well [23–25].
2.3 Interlayer coupling

This section deals with the magnetic coupling between two ferromagnets separated by a thin nonmagnetic layer. It mainly serves as an introduction to chapter 6, that discusses the interlayer coupling in the EuS/PbS/EuS system. We will explain in chapter 6 that interlayer coupling can be a useful mechanism to modify the magnetic switching fields of spin filter layers in devices. A short review will be given on the coupling mechanisms that govern interlayer coupling, focussed on the mechanisms that might be of importance to semiconductor systems. In chapter 6 these mechanisms will be used for comparison with experimental data.

Interlayer coupling became an important field of research in the mid of the 1980’s after the improvement of the fabrication of thin magnetic layered structures. Until then, this type of research was hampered by difficulties in producing nanometer-thick pinhole-free layers. The first clear demonstration of interlayer coupling was the observation of antiferromagnetic coupling in Fe/Cr/Fe in 1986 [48]. The initial research on interlayer coupling focussed on metallic multilayers. With the discovery of the so-called giant magnetoresistance effect for metallic multilayers in 1988 [1, 2] important applications arose for these systems.

Nowadays, interlayer coupling in metallic systems has been thoroughly investigated for several materials [49]. The theoretical understanding of the mechanism behind the interlayer coupling in metals has two equivalent representations. In one representation the coupling is mediated by the spin polarization of free carriers via exchange interaction with the magnetic layers, a special case of the Ruderman, Kittel, Kasuya, and Yosida (RKKY) interaction [50–52]. Alternatively, the interlayer coupling can be described as a result of the quantum interference of conduction electron waves in the spin-dependent potential of the multilayer, known as the quantum interference model [53, 54]. The RKKY interaction energy $J_{RKKY}$ is given by [55]:

$$J_{RKKY} \propto \frac{\cos(2k_F z)}{z^2}$$

where $z$ is the distance between the two magnetic layers and $k_F$ is the wave vector of electrons at the Fermi level. An important feature of the RKKY interaction is its oscillatory nature as a function of the Fermi vector of the free carriers and the thickness of the nonmagnetic spacer layers. RKKY also predicts that the coupling strength decreases quadratically with the distance between the magnetic layers. Details of the theory of interlayer coupling in metallic systems can be found in several reviews [49, 53, 55–57]. Here, it is important to notice that this mechanism relies (in both viewpoints) on an indirect exchange interaction via free charge carriers in the material.

While the interlayer coupling in metallic multilayers is quite well understood, only little is known about the coupling in structures containing semiconductors and insulators. For the interlayer coupling of two ferromagnets across a nonmag-
netic semiconductor layer the carrier concentration is generally too low to support the RKKY mechanism [58, 59]. Therefore, several alternative models were developed to describe the physical origin of the observed interlayer exchange coupling. For systems consisting exclusively of semiconductors these models were reviewed by Kacman [60].

The first type of system that is considered is based on metallic ferromagnets and only the spacer layer is semiconducting. With the development of magnetic tunnel junctions by Moodera et al. in 1995 [3] also these systems consisting of two metallic layers separated by a thin insulating layer became of interest. First observations of an unambiguous antiferromagnetic interlayer exchange coupling across an insulator came from Faure-Vincent et al. [61] in a fully epitaxial system of Fe/MgO/Fe on MgO(100). The coupling can be theoretically understood as originating from a spin-polarized tunnel current through the barrier as described by Slonczewski [62] and can also be described within the framework of the aforementioned quantum interference model by Bruno [54]. The magnitude and the sign of the interlayer exchange coupling in such systems is believed to depend on the barrier height and the exchange splitting of the bands in the ferromagnet [54, 62]. Recently, Zhuravlev et al. [63] showed theoretically that the interlayer coupling in this type of system can also be enhanced by localized states in the barrier region due to impurities and defects.

For heavily doped semiconductor systems the coupling can still be understood within a modified version of the RKKY interaction picture, the Zener model. In III-V diluted magnetic semiconductor heterostructures, like GaMnAs/GaAs/GaMnAs, the coupling is mediated by the holes in the valence band [64, 65], see also figure 2.4a. Jungwirth et al. calculated the coupling energy of such systems within a mean-field framework [59]. The coupling is expected to oscillate with the interlayer thickness and the carrier concentration, starting with a ferromagnetic interaction for thin spacer layers and low carrier concentrations, as is the case in metallic structures. At realistic interlayer thicknesses, very high carrier concentrations are needed to obtain antiferromagnetic coupling (> $10^{20}$ cm$^{-3}$ for a spacer of 3 nm).

Another possible description originates from a model that describes the interaction between the localized magnetic moments in intrinsic diluted magnetic semiconductors. This so-called Bloembergen-Rowland model is based on virtual excitations in the semiconductor. A virtual excitation is based on the fact that the electron wavefunctions do not have to be pure and stationary for finite time intervals. As a result, the electron wavefunction can be a mixed state of valence and conduction band contributions. Dugaev et al. [66] used this coupling mechanism to explain interlayer coupling of two ferromagnetic semiconductors across a nonmagnetic quantum well. They assumed the magnetic moments of the ferromagnetic semiconductor layer to interact by exchange coupling via such virtual excited states in either the conduction or the valence band of the quantum well, as
Figure 2.4: (a) Schematic band structure of a heavily p-doped semiconductor ferromagnet - spacer - ferromagnet trilayer. The localized spins in the ferromagnet are exchange coupled to those of the free holes in the valence band, thus providing an indirect exchange coupling across the nonmagnetic spacer.

(b) Schematic presentation of indirect Bloembergen-Rowland type interlayer coupling in a semiconductor quantum well structure. In the nonmagnetic quantum well a charge carrier is virtually excited, creating a virtual electron and hole. The spins in the ferromagnetic semiconductor can both exchange couple to this virtual electron and hole.

(c) Schematic presentation of indirect interlayer coupling between two ferromagnetic semiconductors separated by a nonmagnetic semiconductor layer, if the coupling is mediated by shallow donor impurities in the nonmagnetic layer.

Illustrated in figure 2.4b. The calculation was performed by first calculating the coupling energy of individual spins at opposite sides of the well, followed by an integration over all spins. The result is a coupling that is always of ferromagnetic nature.

For II-VI semiconductor structures, such as MnTe/CdTe/MnTe, interlayer coupling can be explained by exchange interactions with shallow substitutional donor impurities in the (CdTe) quantum well [67–69], see figure 2.4c. Rusin calculated the coupling energy of two magnetic layers intermediated by one donor state and subsequently carried out a summation over all donor states, obtaining a preferential ferromagnetic coupling [69]. A similar result was obtained by Shevchenko et al. [68]. However, this model was developed for the specific donor states present in CdTe.
Chapter 2. Basics

Blinowski and Kacman [70] used a first-principle approach to rigorously calculate the total electronic energy of EuS/PbS/EuS using a tight-binding model. In a tight-binding model the electronic bands of the material are expressed in terms of the atomic orbitals. For PbS Blinowski and Kacman took into account $s$ and $p$ orbitals for both cations and anions as well as several nearest-neighbor and next-nearest-neighbor exchange interactions. For the EuS anions they took into account $s$ and $p$ orbitals, and for the EuS cations $s$ and $d$ orbitals. Again many interactions were taken into account among which the hybridization of anion $p_↑$ with cation $f_↑$ states, thus introducing a spin splitting of the $p$-type valence band. Similarly, exchange interactions with $s$ and $d$ orbitals of the same cation induce the splitting of the conduction band. The parameters were fitted such that the band structure resembled that from earlier calculations [46, 71, 72]. Subsequently, Blinowski and Kacman calculated the difference in total electronic energy for many points in $k$-space of the valence band between layers aligned parallel and antiparallel. The energy of interlayer coupling was then obtained by summing all these energy differences. A non-oscillatory, antiferromagnetic exchange coupling was favorable in EuS/PbS/EuS with a coupling energy decreasing exponentially with the thickness of the PbS spacer [70].

Of the models available, the model by Blinowksi and Kacman [70] together with the tunneling model by Slonczewski, used to describe the coupling in Fe/MgO/Fe [62], are the only two that predict an antiferromagnetic interlayer exchange coupling for all spacer layer thicknesses. The RKKY and Zener model predict a coupling that oscillates between ferromagnetic and antiferromagnetic nature as a function of spacer layer thickness, although for low carrier concentrations the expected coupling is ferromagnetic [59, 64, 65]. The Bloembergen-Rowland mechanism [66] and the shallow-impurity-induced mechanism that is important to MnTe/CdTe systems always lead to a ferromagnetic coupling. In chapter 6 these models will be used to compare with experimental data, focussing in particular on the temperature and spacer layer thickness dependence of the coupling.
Chapter 3

Experimental

For the fabrication and characterization of the samples discussed in the following chapters of this thesis a broad variety of techniques were used. These are all well-known techniques and they will only shortly be discussed in the present chapter. For a detailed discussion references to earlier work will be given.

3.1 Growth techniques

The samples in this thesis have been grown either by sputtering or by evaporation. The structures that consist completely of semiconducting materials, as described in chapters 6 and 7, were evaporated, whereas those with metallic parts were grown by sputtering. These two growth techniques will be discussed below.

Magnetron sputtering

Sputtering is a well-established growth technique, and has been described extensively elsewhere [73]. The principle behind the sputtering process is the bombardment of the material that is to be sputter deposited with noble gas atoms, thereby knocking some of the atoms out of the material. These atoms can be collected on a substrate. In the case of magnetron sputtering, magnetic fields are used to confine electrons close to the surface of the sputter target preventing energy loss from the noble gas plasma due to escaping electrons.

The system that was used here is a Kurt J. Lesker sputter system containing six sputter guns, as described by LeClair [39]. The background pressure is below 1·10^{-9} mbar after baking the system. Argon 6.0 (impurity content below 10^{-4}%) was used as the sputter gas, and the effective total pressure in the sputter machine was typically 10^{-2} mbar during sputtering. The target of the material to be sputtered was put at a large negative potential. The potential difference with the surroundings, that can be varied from 100 V - 1 kV, ionizes the argon, which is subsequently accelerated towards the target material. The collisions of the argon
ions with the sputter target release atoms from the target. The substrate is put at a distance of 95 mm from the sputter gun, which is larger than the mean free path of the sputtered particles, to collect (part of) the sputtered material. It can be cooled down to 80 K or heated up to 700°C.

While most metallic layers can be grown using a DC negative bias at the sputter target, this is not possible for insulating materials such as EuS. The surface of the sputter target would be charged by positive ions, and this charge remains trapped at the insulating EuS surface. EuS can be sputtered by the application of an alternating bias on the sputter target, thereby removing surface charges. The process is called radio frequency (RF) sputtering, a common variation on sputter growth. In this thesis it is used to grow EuS, PbS and Gd; other metals are grown by DC sputtering.

The sputter system allows for the use of in-situ shadow masks. In this way structures with lateral dimensions down to 100 µm can be made. This is used for the fabrication of metallic strips that can act as the electrodes for tunnel junctions. It also allows for the growth of wedge-shaped samples. If the mask is gradually moved along the substrate surface during deposition of a layer, a gradient in the layer thickness occurs, as more material is collected on the parts of the substrate that have longer been uncovered. Similarly, layer thicknesses can be varied for different samples in one batch.

Evaporation of semiconductor layers

The most common method of growing semiconductor systems is to evaporate the materials. The evaporated semiconductor layers discussed in this thesis can be divided into two categories: samples grown by directly evaporating the semiconductor compound, and samples for which the constituting elements were evaporated from different sources. An introduction to these growth techniques is given in reference [74]. Below they will only be shortly resumed.

The EuS/PbS/EuS trilayers mentioned in this thesis, for which the semiconductor compounds were evaporated, were all grown at the Kharkov Polytechnical Institute in Kharkov, Ukraine. The material that is to be grown is heated in a vacuum system, at a background pressure of $10^{-7} - 10^{-8}$ mbar. The PbS is evaporated from an electrically heated tungsten boat. The substrate is facing the PbS at a distance closer than the mean free path of the evaporated PbS, which is much larger than the typical dimensions of the vacuum equipment. In the case of EuS the standard thermal heating is not applied, as the melting point of EuS is very high (> 2500°C) and the vapor pressure is low. Instead, the EuS is heated with an electron gun. The temperature of the substrate can be tuned over a range of temperatures, but it is kept at 350°C.

The alternative approach, viz., growth by evaporation of the separate constituents, was used for the EuGdTe layers discussed in chapter 7. These samples
were all grown by molecular beam epitaxy (MBE) at the Institute of Physics of
the Polish Academy of Sciences in Warsaw. In a MBE setup the materials to be
deposited are heated in effusion cells that are screened by liquid nitrogen shields.
The facility in Warsaw consists of 7 effusion cells, containing several materials
among which Eu, Gd and Te$_2$ (tellurium). Heating occurs by a tungsten wire
element and the temperature of the effusion cell can be accurately controlled to
set the evaporation rate. The substrate is mounted in a central position such that
parallel deposition from all effusion cells is possible within a range of substrate
temperatures.

3.2 Characterization techniques

A whole range of characterization techniques was used. The most important
techniques are briefly resumed here, with references to more detailed descriptions.

X-ray diffraction

X-ray diffraction (XRD) is used for two reasons. First, it provides information
about the crystallographic properties of the material. Second, it can be used to
determine the thickness of thin layers. The principle of XRD is the interference
of X-rays that are reflected at consecutive planes in the crystal. Only for cer-
tain angles of incidence of the X-rays the path between the planes is such that
constructive interference occurs. The angles of incidence at which maxima in the
reflection intensity occur can thus be related to the distance between the planes
as is described within the well-known Bragg’s law.

It is important to have some information on the grain size of the sputtered
EuS layers. From the width of the peaks in the XRD spectrum the size of
the crystallites in the direction perpendicular to the sample surface $s$ can be
determined using the so-called Scherrer formula:

$$ s = \frac{0.9 \lambda}{\text{FWHM} \cos \theta} $$

in which $\lambda$ is the wavelength of the X-rays (1.5406 Å for the Cu source used),
$\theta$ is the angle of incidence of the X-rays with respect to the sample surface,
and FWHM is the full width at half maximum of the diffraction peak under
consideration in radians. The Scherrer formula can be understood as follows. For
X-rays reaching the samples at angles close to those obeying the Bragg condition
the difference in path length for rays reflected at two neighboring planes is still
close to one wavelength. As a result the first plane that scatters a wave exactly out
of phase compared to the top plane will already be far away inside the crystal.
Thin crystals or thin crystallites may then be too small to obtain completely
destructive interference, and the peak in the diffraction spectrum will get a finite
width with a FWHM as determined by the Scherrer formula. Several textbooks discuss the physics behind XRD; an extensive treatment is for instance given by Cullity [75].

Grazing incidence XRD is also used to determine layer thicknesses for thin layers of 100-1000 Å. The diffraction pattern is then measured in a range of angles where it is governed by reflections from different interfaces in the sample instead of reflections from all the atomic planes. As a consequence the refractive index in the material has to be taken into account and the diffraction pattern is no longer described by Bragg’s law. Therefore, layer thicknesses are determined from a simulation of the (low-angle) diffraction pattern [76].

**X-ray photoelectron spectroscopy**

X-ray photo-electron spectroscopy or XPS is used in this thesis to obtain information on the charge of the Eu ions. The general principle of XPS is that the material is irradiated by X-ray radiation. The monochromatic X-rays excite electrons from electron bands at various energies into the vacuum. These electrons are detected after passing an energy analyzer to measure their kinetic energy. The difference between the photon energy of the incident X-rays and the measured kinetic energy of the escaping electron equals the binding energy of the electron. In this way the density of states of a material can be measured from the valence band, above which no electrons are available to be excited, down to the energy level that is exactly the photon energy below the vacuum level.

XPS is a surface sensitive technique. Although the penetration depth of the X-rays can be high, the limited electron escape depth makes the technique sensitive to the top layer only. The electron escape depth various with the material, but it is often in the order of 1-10 nm. An extensive treatment of the XPS technique is for instance given by Briggs [77].

XPS is commonly used to identify elements from the energy levels of their core levels. In this thesis advantage is taken from the fact that the energy of a core level with respect to the vacuum level depends on the charge of the atom. More specifically, for EuS the position of the Eu 5d band depends on the charge state of the Eu ion. As a consequence Eu$^{2+}$ and Eu$^{3+}$ can be distinguish from each other, and their relative abundance can be determined.

**SQUID**

The standard approach to measure a small magnetic moment is by using a Superconducting Quantum Interference Device (SQUID). The principle of a SQUID, together with the required electronic circuitry has been described extensively [78, 79]. In short, the technique relies on the quantization of magnetic flux through a superconducting ring that contains a small interruption, a so-called Josephson
junction. The flux through this ring, which is the actual SQUID, depends in a typical fashion (with abrupt jumps) on the externally applied flux, including a flux resulting from the presence of a sample. The SQUID ring is coupled by a mutual inductance at one side to superconducting pick up coils that sense the flux originating from the sample, and on the other side to electronic circuitry. A radiofrequency current is driven through the electronics, and the related voltage that depends on the flux through the SQUID ring, and thus on the magnetic moment of the sample, can be monitored. The electronics contain a feedback system that keeps the system at a fixed state after a change of the magnetic flux through the SQUID ring. The feedback voltage is then a measure of the flux and the magnetic moment.

The SQUID system that was used, is a Quantum Design MPMS-5S magnetometer, that can measure magnetic moments with a sensitivity of 0.2 nAm$^2$ at a magnetic field up to $4.4 \cdot 10^3$ kA/m in a temperature range from 1.7 K to 400 K.

**MOKE**

An alternative method for measuring magnetization is based on the magneto-optical Kerr effect (MOKE). As compared to SQUID, MOKE is less sensitive and does not provide a direct measure of the absolute magnetic moment, since it is only proportional to the layer magnetization. It has, however, the advantage that it is much faster. Furthermore, a MOKE measurement is confined to a small laser spot, providing information on the local magnetization in the spot, whereas with SQUID the global magnetic moment of the entire sample is measured.

A description of the MOKE technique is given by Bader [80], here only the physical principle will be discussed. MOKE is an optical technique, relying on the change in light polarization upon reflection at a magnetic surface. Usually a laser beam of a known polarization is focused on a magnetic surface. Due to the spin dependence of the band structure in combination with the presence of spin-orbit coupling, the probability for optical transitions will depend on the (circular) polarization of the light. Thereby, the polarization of the reflected beam differs from that of the incident one. The rotation ($\vartheta$) and the change in ellipticity ($\epsilon$) of the polarization of the laser beam are a function of the complex dielectric tensor and the layer thickness. Here, it is just mentioned that the Kerr effect can be considered proportional to the magnetization of the layer. In general, sharp resonances appear for photon energies near the band gap causing a strong dispersion as a function of the wavelength of the incident light. At the wavelength that was used, the Kerr effect due to EuS was well measurable.

For a bilayer the total Kerr rotation can be written as the sum of the contributions due to the separate layers:

$$\vartheta = a_1 M_1 + a_2 M_2.$$  \hspace{1cm} (3.2)
Here $\vartheta$ is the total Kerr rotation upon reflection at the multilayer. $M_1$ and $M_2$ are the magnetizations of the two layers with proportionality constants $a_1$ and $a_2$, respectively. A similar relation is valid for the Kerr ellipticity, and both equations can be extended with extra terms to represent more layers. As the sign of the Kerr rotation of a layer can be either positive or negative, which depends on the exact complex refractive index of the material, also the proportionality constants can be positive or negative. As a result the Kerr rotation of two ferromagnetic layer magnetized in parallel can be either of the same or of opposite sign.

The MOKE setup that was used has a wavelength of 632.8 nm and a laser spot size of 100 $\mu$m. It allows for measurements from 5 K to 300 K at a magnetic field up to 800 kA/m.

**Atomic Force Microscopy**

In this thesis a few Atomic Force Microscopy (AFM) images are presented. AFM is a surface imaging technique, that relies on the forces between the surface and a sharp tip. The resolution is determined by the sharpness of the tip and the mechanical movement of the tip by piezo elements. In practice, the tip is mounted on a cantilever, of which the exact deflection towards or away from the substrate is determined from the position of a laser beam reflected from the cantilever. The pictures displayed in this thesis were measured in the so-called tapping mode. In the tapping mode the tip is scanned at a small distance from the surface; the cantilever is made to oscillate and regularly “hit” the surface (“tapping”). The force between the tip and the surface, a combination of attractive Van der Waals force and repulsive atomic forces, that can be considered a function of the tip-surface distance, influences the oscillation frequency and amplitude. If these are kept constant by raising and lowering the tip during a scan, the height of the tip is a measure of the height of the surface. Surface characterization techniques are extensively treated by Magonov, including an extended discussion on the AFM technique [81].

**Electrical characterization**

The electrical measurements described in this thesis are rather standard. All electrical measurements were performed on tunnel junctions, in which two perpendicular electrode strips are separated by the insulating tunnel barrier. Each electrode contains current and voltage leads. For a measurement the current is set at a fixed value and the voltage is measured subsequently. In our home-built setup the current can be set from 0.1 nA to 10 $\mu$A, and junctions with resistances up to 10 G$\Omega$ can be measured. The magnetic field can be swept from $-10^3$ kA/m to $10^3$ kA/m. The setup is placed in a helium flow cryostat enabling measurements at temperatures from 2 K to room temperature. Electrical measurements
on tunnel junctions, as well as the actual setup, are described in more detail by
LeClair [39].
Chapter 4

Magnetoresistance based on a EuS spin filter and a ferromagnetic electrode

A spin filter as introduced in chapters 1 and 2 can be applied as a component in a magnetoresistance device. In order to obtain a magnetoresistance effect the spin filter can be combined with either another spin filter, which will be the topic of chapter 5, or with a single ferromagnetic electrode. In both cases the resistance is expected to depend on the mutual magnetic alignment of the two ferromagnetic layers. This chapter deals with magnetoresistance devices based on the combination of a spin filter with a single ferromagnetic electrode. Such a magnetoresistance device serves two purposes: first, it serves as a straightforward proof of the principle of spin filtering; second, the magnetoresistance itself may be attractive for applications, such as magnetic memories or field sensors. Compared to “common” metallic ferromagnets a spin filter has the advantage that it can in principle be used to obtain a current that is completely polarized. However, since no ferromagnetic semiconductor is currently available at room temperature, and even the growth of thin insulating layers that are only ferromagnetic at cryogenic temperatures is not yet well controlled, the development of such a device is far from trivial.

The chapter is organized as follows. First, the physical principles behind a magnetoresistance device based on the combination of a spin filter and a ferromagnetic electrode will be discussed. Attention will be given to the corresponding demands on the device layout and the choice of materials. Several possible systems will be discussed, with extra attention for promising candidates such as Co/AlO$_x$/EuS/Ta and Al/EuS/Gd. A EuS tunnel barrier optimization study will be presented, followed by one of the main topics of this chapter, which is a report of resistance measurements of samples in which the improved EuS was implemented. In this part, also a survey will be given of sample layouts that did or
did not lead to magnetoresistance effects. Finally, the last part of the chapter is devoted to an investigation of interlayer coupling between adjacent EuS and Gd layer, where surprisingly the expected strong ferromagnetic coupling is absent.

Part of this chapter has already been published in the Journal of Applied Physics [82].

4.1 Introduction

The most important obstacle for driving a highly spin-polarized current from a metal into a semiconductor is the large difference in resistivity, the so called impedance mismatch [37] as was already discussed in chapter 2: the spin-dependent resistivity of the metal is masked due to the large resistivity of the semiconductor. To avoid the problem of impedance mismatch, Rashba suggested that a high-resistive tunnel barrier should be introduced at the metal-semiconductor interface [10]. In this way the current would be determined by the tunnel contact from the metal to the semiconductor and therefore, according to equation 2.13, indeed depend significantly on the spin-dependent density of states in the metal. An alternative approach is to replace the ferromagnetic metal and nonmagnetic tunnel barrier with a spin-filter barrier, where the spin filter is a semiconductor with different barrier heights for electrons of both spin orientations, as defined in chapter 1.

A spin filter can be created using a ferromagnetic semiconductor, since below the Curie temperature the magnitude of the bandgap depends on the spin orientation. As the electron transmission of a tunnel barrier depends exponentially on its height and thickness, according to equation 2.12, the spin-filter efficiency of a ferromagnetic semiconductor tunnelling barrier depends exponentially on the difference in barrier heights for the two spin directions and on the barrier thickness. Therefore the efficiency can be tuned to any desired value, allowing near 100% (pseudo half-metallic) efficiency of spin filtering for very thick barriers. Another advantage of these spin filters is that their efficiency does not originate from interface effects, in contrast to what is the case for standard tunnel junctions [83].

Observation of the spin filtering effect

The first sign of spin dependent transport in a magnetic semiconductor was obtained by Esaki et al. [84] in internal field emission or Fowler-Nordheim tunneling experiments. They studied the current-voltage characteristics of a EuS layer sandwiched between two metallic electrodes. The large decrease in resistance observed below the EuS Curie temperature was explained by assuming tunneling transport. In this scenario the tunnel barrier height is determined by the bottom of the conduction band and is lowered, at least for electrons of one spin orientation, upon the magnetic ordering of the EuS.
Chapter 4. MR based on a EuS spin filter and a ferromagnetic electrode

Figure 4.1: Normalized conductance curve for the original spin-polarized tunneling measurement by Hao et al. [85] for an Al/EuS/Al tunnel junction. From the relative peak heights a current spin polarization of 85% at an effective field of 1.9 T was inferred.

A quantitative analysis of spin filtering can be obtained in a combination with either a superconducting [85] or ferromagnetic [5] electrode. Hao et al. [85] combined a barrier of the magnetic semiconductor EuS with two superconducting aluminium electrodes to perform a superconducting tunneling spectroscopy measurement. The technique takes advantage of the BCS density of states of the superconductors. A tunnel current requires filled electron states of one electrode to be at the same energy level as empty states in the other electrode. Because of the superconducting band gap this requirement is only fulfilled for certain voltages across the junction. The result is a conductance - voltage curve with only two conductance peaks, i.e. for voltages at which the conduction band at one side of the tunnel barrier is at the same energy as the valence band at the other side. These peaks are Zeeman split if a magnetic field is applied; this situation is plotted in figure 4.1. This magnetic field can be externally applied, but in the case of a ferromagnetic barrier also exchange interaction with the magnetic tunnel barrier causes the conductance peaks to be spin split. From the relative peak height the polarization can then be derived.\footnote{In figure 4.1 a small fifth peak (near zero bias) is present related to a small conductance if the conductance bands at both sides of the barrier are aligned in energy. However, this peak will not be discussed further.} The method and the measurements are described by Hao et al. [85]. Although the polarization is probed with the density of states of a superconductor, as in ordinary spin polarized tunneling mea-

\[ T = 0.49 \text{ K} \]
\[ H = 0 \text{ kA/m} \]
measurements on metals [86, 87], these measurements should not be confused with each other, since the source of spin polarization is different. Figure 4.1 shows a measurement from the original paper by Hao et al. [85]. From the relative peak height in this measurement a tunneling spin polarization was derived of 85% for a barrier of 33 Å thickness at an effective field (due to exchange interaction with the neighboring magnetic EuS layer) of 1.9 T. Recently, a similar experiment was performed using a EuO spin filter instead of EuS, revealing a spin polarization of the tunnel current of 29% at a barrier thickness of 14 Å [88]. After correction for the spin filter thickness it still appears that EuS is a more effective spin filter than EuO. However, the research on spin filtering is still in an early stage, in which the exact efficiency of the spin filter is not yet of the highest importance.

Probing the spin filter effect with a ferromagnetic electrode

Combination of a spin filter with a ferromagnetic electrode (and one nonmagnetic electrode) should lead to a magnetoresistance effect. From the magnetoresistance it is not only possible to derive the efficiency of the spin filter and thus demonstrate its functionality, but the effect in itself also allows for interesting applications. Possibilities include field sensors and magnetic memories in a similar fashion as for magnetic tunnel junctions based on two ferromagnetic electrodes [7]. A specific advantage of the use of spin filters in these devices is the expected magnitude of the magnetoresistance effect due to the high polarization. Moreover, devices based on spin filters are expected to be less dependent on interface properties than normal magnetic tunnel junctions.

![Figure 4.2: Schematic representation of the magnetoresistance effect for a spin filter tunnel junction with a metallic ferromagnetic counterelectrode. Dependent on whether the spin filter (SF) and the ferromagnetic electrode (FM) are aligned in parallel or antiparallel, electrons of the spin orientation that experiences the lowest tunnel barrier height can either tunnel into majority or minority states in the ferromagnetic electrode.](image)
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In order to obtain a simple equation that describes the magnetoresistance of a spin filter tunnel junction, as is depicted in figure 4.2, the general expression for a metal-insulator-metal tunnel junction is taken as a starting point. For convenience, the equation for a tunnel current through such a junction, equation 2.13, that originates directly from Fermi’s Golden Rule, is repeated here:

\[
I(V) = \int_{-\infty}^{+\infty} \rho_l(E)\rho_r(E + eV)|M|^2 f(E)[1 - f(E + eV)]dE. \tag{4.1}
\]

Equation 4.1 is applied separately to electrons of each spin orientation. The density of states of the ferromagnetic electrode is thus taken to be spin dependent. Moreover, since the tunnel barrier height is different for spin up and for spin down electrons, the squared matrix element that describes the overlap of wavefunctions from both sides of the barrier (to which the tunnel probabilities \(T^\uparrow\) and \(T^\downarrow\) are proportional) is spin dependent too. The integrand in equation 4.1 is close to zero if the argument of the Fermi function \(f(E)\) exceeds the Fermi energy or if the argument of \(f(E + eV)\) is much lower than the Fermi level, since at these energies there are either no electrons available or empty states to tunnel into. As a result, the integration only has to be taken over a small energy band, in which the densities of states \(\rho_l\) and \(\rho_r\) can be assumed to be constant. For small applied biases the integral in equation 4.1 can be written as a multiplication of the bias energy \(eV\) with the density of states at the Fermi energy. The tunnel current through the spin filter barrier then reduces to:

\[
I(V) = I^\uparrow + I^\downarrow \simeq \rho_l^\uparrow \rho_r^\uparrow T^\uparrow V + \rho_l^\downarrow \rho_r^\downarrow T^\downarrow V \tag{4.2}
\]

in which the total current is split into spin-up \(I^\uparrow\) and spin-down \(I^\downarrow\) contributions.

The tunnel current for the spin filter and the magnetic electrode in parallel and antiparallel alignment, respectively, as depicted in figure 4.2, is written as:

\[
I_P \simeq \rho_l T^\uparrow \rho_r\text{maj} V + \rho_l T^\downarrow \rho_r\text{min} V \tag{4.3}
\]

\[
I_{AP} \simeq \rho_l T^\downarrow \rho_r\text{min} V + \rho_l T^\uparrow \rho_r\text{maj} V. \tag{4.4}
\]

As in chapter 2, \(\rho_l\) and \(\rho_r\) denote the density of states of the electrodes. For the ferromagnetic electrode the subscripts “maj” and “min” indicate majority and minority spin electrons, respectively. The sum of the densities of states for spin-up and spin-down electrons is of course the total density of states in the magnetic electrode. Moreover, the polarization of the electrode \(P_m\) can be introduced as:

\[
P_m = \frac{\rho_{\text{maj}} - \rho_{\text{min}}}{\rho_{\text{maj}} + \rho_{\text{min}}}. \tag{4.5}
\]

Analogously, following the definition by LeClair [39], the polarization of the spin filter is written in terms of its transmission, or, equivalently, of its conduction, for electrons of both spin orientations:

\[
P_f = \frac{T^\uparrow - T^\downarrow}{T^\uparrow + T^\downarrow}. \tag{4.6}
\]
With the notations above the magnetoresistance ratio of a spin filter tunnel junction can be written as

\[
\text{MR} = \frac{R_{AP} - R_P}{R_P} = \frac{G_P - G_{AP}}{G_{AP}} = \frac{T_\uparrow \rho_{maj} + T_\downarrow \rho_{min} - T_\uparrow \rho_{min} - T_\downarrow \rho_{maj}}{T_\uparrow \rho_{min} + T_\downarrow \rho_{maj}} = \frac{2P_f P_m}{1 - P_f P_m}.
\]

(4.7)

This result is similar to the well-known Jullière formula (equation 2.17) for magnetic tunnel junctions with a nonmagnetic barrier and two ferromagnetic electrodes. This can be explained as follows: For each spin channel the barrier transmission shows up linearly in the conductance of the spin filter tunnel junction, as can be seen in equation 4.2. This is analogous to the dependence of the tunnel current through a regular magnetic tunnel junction on density of states of the second magnetic electrode, causing the resulting expressions for the magnetoresistance to be similar.

LeClair et al. [5, 39] combined a EuS spin filter layer with a ferromagnetic Gd electrode to create a spin filter tunnel junction. Their result is shown in figure 4.3. When looking at figure 4.3 it can be seen that at high magnetic fields, where the spin filter and the magnetic electrode should be aligned in parallel (cf. the inset of the figure), the resistance of the device is minimal. When the field is swept, at a certain moment the magnetization of one of the layers switches, resulting in an antiparallel configuration of the magnetizations, in agreement with the decreased total magnetization in the hysteresis curve in the inset. This is accompanied by an increase of the resistance of the device. If the field is swept further, also the second magnetic layer switches, restoring the original parallel alignment of the magnetizations. The resistance decreases correspondingly to its original value. What can be noticed immediately is the magnitude of the magnetoresistance effect of over 100%, which was at the time of the experiment higher than what was obtained for magnetic tunnel junctions with a nonmagnetic barrier and two ferromagnetic electrodes. The exact shape of the curve, however, is not completely understood. It is clear that the effect diminishes with increasing temperatures and finally vanishes at \(T = 30\) K, above the Curie temperature of EuS, indicating that the EuS spin filter is responsible for the magnetoresistance effect.

Recently, spin filter electronics started to receive great interest. An experiment similar to the one by LeClair et al. was performed by Gajek et al. [23]. The main difference with the experiment by LeClair et al. is the choice of materials. Gajek et al. used a BiMnO\(_3\) spin filter, allowing for combination with a half-metallic La\(_{2/3}\)Sr\(_{1/3}\)MnO\(_3\) (LSMO) electrode. Moreover, BiMnO\(_3\) has a Curie temperature of 105 K, exceeding that of EuS. At low temperatures (\(T = 5\) K) the exchange splitting of the conduction band is estimated to be 0.5 eV. They observed a large magnetoresistance effect, of about 50% at 3 K, confirming the feasibility of spin filter tunnel junctions.
Figure 4.3: Magnetoresistance of a Al/EuS/Gd spin filter tunnel junction at various temperatures below and above the EuS Curie temperature of 16.8 K as observed by LeClair et al. [5, 39]. The inset shows the magnetic hysteresis curve of a sample with the same layer structure.

Lüders et al. [24, 25, 89] used NiFe₂O₄ as a spin filter tunnel barrier (the exchange splitting of the barrier height is claimed to be 1.5 – 2.5 eV). As the ferromagnetic electrode they used LSMO. The NiFe₂O₄ was grown epitaxially on the LSMO bottom electrode on a SrTiO₃ (STO) substrate. Au was used as the top electrode. The LSMO was grown by pulsed laser deposition and the NiFe₂O₄ by target-facing-target RF sputtering, in which the substrate is positioned under an angle with two sputter targets. The magnetoresistance that is achieved reaches 50% at 4 K. Chapline et al. [26] combined a CoFe₂O₄ ferromagnetic insulator with half-metallic Fe₃O₄. They obtained tunneling current-voltage characteristics but did not show any magnetoresistance curve yet.

The structures described in this chapter are all based on sputter-grown EuS as the spin filter layer. EuS was already introduced in chapter 1. Summarizing, EuS is a well-studied ferromagnetic semiconductor [18] \(a = 5.97 \text{ Å}, T_C = 16.8 \text{ K}, E_c - E_F = 1.65 \text{ eV}\), which exhibits a spin splitting of the conduction band of
up to 0.36 eV below $T_C$. The splitting of the conduction band was observed in field emission experiments \[84\], and was also determined using superconducting electrodes \[85\] and by combination with a single ferromagnetic electrode \[5\], as was discussed above. Its low Curie temperature makes EuS unsuitable for electrical device applications, but because of the earlier research available it is still an excellent material for a study of the physics behind spin filtering.

Despite the reported encouraging results \[5, 39, 85\], incorporation of EuS in (spin) electronic devices is not straightforward. Care has to be taken that the EuS does not oxidize during the growth of the structure and that the electrode material does not diffuse into the EuS. Another problem could be the roughness of the EuS tunnel barrier which could lead to pinholes for barrier thicknesses of only a few nm \[90–92\]. Moreover, as mentioned before, LeClair’s results shown in figure 4.3 are far from trivial. While the hysteresis curve in the inset of the figure shows only two steps, originating from the switching of the two individual magnetic layers, the magnetoresistance curve shows a more complex behavior, with steps that do not appear to be correlated with the magnetic behavior of the layers present. This is in contrast with the simple picture of two homogeneously magnetized ferromagnetic layers that is the desired model system to demonstrate the spin filter effect. Additionally, since the two ferromagnetic layers in this structure, EuS and Gd, are in direct contact, a strong (ferromagnetic) coupling is expected. However, remarkably, in the hysteresis curve (inset of figure 4.3) independent switching of the two layers is observed. In view of this peculiar behavior a study of the structural and magnetic properties of EuS spin filters is desired.

This chapter

In this chapter first a systematic optimization study of the EuS spin filter barrier for magnetoresistance devices is presented. It will be shown that, with respect to growth parameters, for application as a spin filter tunnel barrier the best EuS films are obtained by growing at a substrate temperature of 200°C and afterwards annealing at a higher temperature (430°C). Next, the issue of interlayer mixing and material compatibility will be addressed. Then the optimized barriers will be used to grow full magnetoresistance devices, starting with EuS spin filters with Gd as the top electrode. For instance, for some of the Al/EuS/Gd structures a magnetoresistance is observed with a clean, single-stepwise switching behavior. Also some attention will be given to the feasibility of alternative systems based on EuS as the spin filter. However, only in systems containing a Gd electrode combined with the EuS spin filter a magnetoresistance effect was observed. Finally, the magnetic properties of the bilayered EuS/Gd system are investigated in more detail. It will be shown that the independent magnetic switching of the two layers can be explained by a nonmagnetic layer at the interface.
4.2 Sample structure and preparation

A spin filter tunnel junction consists of a ferromagnetic semiconductor or insulator and one ferromagnetic and one nonmagnetic electrode. As mentioned before, EuS is used as the spin filter material. Since the spin filter layer is of crucial importance to the working of a spin filter tunnel junction, the growth of EuS layers will be reviewed here.

At present, evaporation is the most widely used growth method for EuS thin films [91, 93–95]. They can be grown epitaxially on KCl (100) or PbS (100) at a relatively low substrate temperature of 520 K and at a background pressure of $10^{-6} - 10^{-7}$ mbar [93, 95]. On other substrates textured polycrystalline EuS can be grown [85, 91, 94]. Demokritov et al. [91] and Guilaran et al. [94] obtained EuS layers with high defect densities, that showed defect-induced enhanced Curie temperatures, while Hao et al. [85] obtained high-resistive EuS that could be used as a tunnel barrier. Alternatively, EuS can be grown by RF magnetron sputtering as was done by LeClair et al. [5, 82], who showed that a sputter-grown EuS spin filter can lead to a magnetoresistance effect. The surprising result that EuS can successfully be grown by sputtering offers the opportunity to use in-situ shadow masks, enabling the controlled variation of the EuS layer thickness within one batch and allows for high production rates. Because of this, sputtering may provide the easiest way to perform a full study of the spin filtering effect. The remainder of this chapter will deal with sputtered EuS layers only.

Sputter growth of semiconducting EuS requires a pressure below $10^{-8}$ mbar for the sputter rates that are typically used, since EuS layers grown at higher pressures have generally too low resistances, and are not suitable as a barrier layer. To achieve these pressures, baking of the system is required. For the same reason the EuS target always has to be presputtered for several hours, and the substrate has to be degassed (typically 1 hour at 500-650°C) before the EuS layer can be grown.

With respect to the sample structure, many different sample layouts are possible. The ferromagnetic electrode could be either the top or the bottom electrode and the choice of the electrode materials is still free. As a starting point the Al/EuS/Gd system, the subject of the work by LeClair et al. [5, 39], is taken. The complete sample structure of this junction is Si/SiO$_x$/Ta/Al/EuS/Gd/Al, in which EuS, Al and Gd form the heart of the device as the spin filter and the bottom and top electrode, respectively. The Ta is added as a seed layer to promote a smooth growth of the Al bottom electrode. The top Al layer is a capping layer to protect the Gd top electrode from oxidizing. The growth details for samples with other layer sequences will be given when they are discussed later in this chapter.

All samples are completely grown by conventional ultra-high-vacuum sputtering techniques with in-situ shadow masks, see also chapter 3. Generally, oxidized
Si(100) wafers were used as substrates. The metallic layers were grown by DC sputtering, at growth rates of 0.5 - 1.5 Å/s. The EuS layers had thicknesses from 50 Å to 500 Å and the growth rate (for RF sputtering) was kept constant for all samples at 0.26 Å/s while growth temperatures were varied between 50°C and 450°C. After growth some of the EuS layers were annealed at 400-450°C.

Both tunnel junctions (0.5 × 0.5 mm²) and simple layered samples have been produced, depending on the characterization technique to be applied. The tunnel junctions always consist of two crossed, perpendicular, 0.5 mm wide electrodes separated by a planar (EuS) barrier. Tunneling takes place only at the crossing where the two electrodes are only separated by the thin EuS tunnel barrier, leading to the junction area of 0.5 × 0.5 mm².

4.3 Optimization of the EuS tunnel barrier

The spin filter layer is the crucial component of any spin filtering device. However, although information on the bulk properties is available, not much is known about the growth of a EuS semiconducting magnetic thin film. Moreover, the magnetic switching of the device produced by LeClair et al. has not been understood, as described in section 4.1. In this section the characterization of a EuS layer is reported and it is discussed how the quality of the spin filter layer is influenced by variation of the growth parameters. First, the crystalline structure of the EuS will be evaluated. Next, in a systematic XPS study the dependence of the chemical properties of EuS on both the growth temperature and annealing is investigated, followed by a discussion of interlayer mixing and material compatibility, also from chemical point of view. Then, the magnetic properties of the EuS layers will be verified for the same samples as in the XPS study. Finally, the magnetic properties and chemical quality will be compared and a growth procedure (temperature, annealing) will be chosen.

A first start is to check the crystalline quality of the EuS layers. Therefore, X-Ray Diffraction (XRD) measurements have been performed on a 500 Å layer of EuS. The resulting spectrum is shown in figure 4.4. The main EuS peak that is observed originates from a (200) reflection, and also the higher-order (400) and (600) peaks can be discerned. A EuS (220) peak is absent and the relative area of the EuS (111) peak with respect to the EuS (200) peak is only 3%, which is 20 times lower than it would be for EuS powder. Since rotation of the sample around its normal reveals no single-crystalline behavior, it can be concluded that the growth of EuS is predominantly (100) textured. The width of the EuS (200) peak in the spectrum is 0.40°. Using the Scherrer formula, equation 3.1, this width can be related to an out-of-plane coherence length of 210 Å, roughly half the film thickness. The rocking curve has a width of about 6.5° (see the inset of figure 4.4), indicating a mosaic structure comparable to the one obtained by Keller et al. for evaporated EuS layers on top of a GaAs substrate [92].
Figure 4.4: X-ray (Cu-Kα) diffraction spectrum of a 500 Å thick EuS layer grown at 400°C on an oxidized silicon substrate. The substrate was tilted 1° in order to attenuate the silicon peaks. Positions of Si and EuS peaks are indicated, although no EuS(220) peak is present. The inset shows the rocking curve for the main EuS(200) reflection, with a silicon reflection on top. 2θ is the angle between the incident X-ray beam and the detector; ω denotes the angle between the incident beam and the sample surface.

Chemical properties of EuS spin filter layers

The stoichiometry and the chemical structure of the EuS layers were characterized by in-situ X-ray photoemission spectroscopy (XPS). In this study the intensity of the core level 3d states of the europium ions [96] was monitored. Since the 3d peaks are at different positions in the XPS spectrum for Eu²⁺ and Eu³⁺ ions due to their different charge, the presence of both ions can be detected independently. In pure, stoichiometric EuS the Eu ion is in a 2+ charge state; the Eu³⁺ is a sign of the presence of paramagnetic, more stable Eu₃S₄. Figure 4.5 shows the results of such a study for EuS samples that were grown at various temperatures for a Si/SiOₓ/PbS(40Å)/EuS(60Å)/PbS(10Å) sample, where PbS is introduced both as a buffer and a capping layer. In the figure it can be observed that for EuS layers sputtered at low temperatures a considerable amount of undesired Eu³⁺ is present, while much less Eu²⁺ can be discerned. Raising the growth temperature causes the Eu²⁺/Eu³⁺ ratio to increase until almost no Eu³⁺ ions can be observed at 400°C. It can thus be concluded that growing at a higher temperature improves the Eu(II)S content.

However, grazing angle X-ray diffraction measurements suggest that the EuS layers grown at 400°C are very rough, typically of the order of 10 Å (RMS). In section 4.7 also AFM images will be presented that show roughnesses of the same order of magnitude. This is in agreement with resistivity measurements on many
Figure 4.5: XPS spectra for Si/SiO$_x$/PbS(40Å)/EuS(60Å)/PbS(10Å) samples grown at various temperatures ranging from 50°C to 400°C. The positions of the Eu$^{2+}$ and Eu$^{3+}$ 3d peaks are indicated.

different junctions incorporating EuS, showing electrical shorts in the EuS barrier layer up to layer thicknesses of 60 Å. Since this high level of roughness was not observed for EuS layers grown at lower temperatures, also layers were grown at relatively low temperatures, that were subsequently annealed in-situ (at 430°C). Figure 4.6 shows XPS spectra for these samples. For comparison also the spectra of samples without annealing are plotted. The annealed samples show a strong decrease of the Eu$^{3+}$ and increase of the Eu$^{2+}$ peak intensities, with respect to their unannealed counterparts (the area of the Eu$^{2+}$ peak compared to the sum of the Eu$^{2+}$ and Eu$^{3+}$ peaks increases by 32%), indicating an improved chemical structure. Since it is unlikely that stable Eu$_3$S$_4$ disappears upon annealing, the presence of Eu$^{3+}$ is probably due to defects instead of substantial quantities of Eu$_3$S$_4$. In either way, the chemical quality of a EuS layer that is annealed after growth at a lower temperature is comparable to that of a sample grown at the anneal temperature. From electrical experiments it appears that the former is less rough than the latter, making it more suitable as a tunnel barrier.

In tunneling devices also the influence of the neighboring layers on the chemical quality of the spin filter is of crucial importance. EuS and its compounds have a reputation of poor compatibility with other materials due to interdiffusion and
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Figure 4.6: The effect of annealing on the XPS spectrum of EuS: solid lines correspond to samples Si/SiO$_x$/PbS(40Å)/EuS(60Å)/PbS(10Å) that were all annealed for 1h at 430°C, differing only in growth temperature. For comparison the dashed lines denote the corresponding nonannealed samples (from figure 4.5).

misfit dislocations [91, 92]. For a first test of electrode - spin filter interaction Al is used as a nonmagnetic and Co as a magnetic electrode. Figure 4.7 shows XPS spectra for EuS layers grown on these two metals. For comparison, also spectra for a few other layer sequences grown on an oxidized silicon substrate are presented: Al/PbS/EuS, EuS, and EuS/PbS. For all these samples the metallic layers were grown at room temperature, and the EuS and PbS layers at 200°C, followed by an anneal step at 400°C. The result can be summarized as follows. The spectra of the EuS layers next to a metallic electrode show a stronger Eu$^{3+}$ peak with respect to the spectrum of EuS sandwiched between PbS layers or EuS grown directly on the bare substrate (SiO$_x$), indicating a higher amount of defect states. However, when comparing the Al/EuS to the Al/PbS/EuS spectrum, it appears that the addition of a thin (40 Å) PbS layer reduces the amount of defects again to a value that is close to the one if no Al would be present (figure 4.6). Thus, either the PbS provides a better diffusion barrier for Al than EuS, or the presence of the Al layer affects only the part (first few nm’s) of the semiconductor that is closest to the interface. In conclusion, growth of a EuS spin filter on a metallic bottom electrode (either Co or Al) instead of either a SiO$_x$ substrate or a PbS layer leads to a lower chemical quality of the EuS. For Al at least, this influence can be avoided by the addition of a thin PbS spacer at the interface.
Figure 4.7: XPS spectrum of EuS for samples varying in structure with different layers at the EuS interfaces. Metallic layers in these samples were all grown at room temperature, the EuS and PbS layers at 200°C. All samples were annealed at 400°C immediately after the deposition of the semiconducting EuS and PbS.

Magnetic properties

Next, the magnetic behavior of EuS is considered. Hysteresis loops of EuS sandwiched between PbS layers are shown in figure 4.8 for structures grown at various temperatures. All loops were measured at 5 K, well below the Curie temperature of EuS (16 K). Starting at a growth temperature of 50°C, at which no ferromagnetic EuS can be discerned, the saturation moment increases rapidly upon increasing the growth temperature to 200°C. For growth temperatures above 200°C only a very small increase can be observed. This is only in partial agreement with the XPS data, that showed an increase in the amount of Eu$^{2+}$ at the cost of Eu$^{3+}$ ions in the whole growth temperature range (see figure 4.5), considering that the Eu$^{2+}$ is responsible for the magnetism in EuS. In other words, while the magnetic moment appears to saturate at a growth temperature of 100-200°C, the amount of Eu$^{2+}$ keeps increasing for growth temperatures up to 400°C. At the end of this section the XPS and SQUID results will be compared more extensively. Although the curves in figure 4.8 do not really suggest this, EuS can have magnetic saturation fields of up to 1 T, so it cannot be excluded that the magnetization of a part of the EuS is not yet saturated.
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Figure 4.8: Hysteresis curves ($T = 5$ K) of the EuS layer in Si/SiO$_x$/PbS(40 Å)/EuS(60Å)/PbS(10Å) structures, grown at substrate temperatures ranging from 50-400°C.

Alternatively, information on the behavior of the EuS magnetic moment can be obtained by studying its temperature dependence. The magnetic moment for a series of field-cooled samples is plotted in figure 4.9. It can immediately be seen that the highest magnetic moment is obtained for samples grown at the highest temperatures. The graph is scaled to the Curie temperature of the EuS layers, which rises gradually from 15.3 K for layers grown at 400°C to 16.8 K for growth at 100°C. The data for the EuS layer grown at 50°C suggest an even higher Curie temperature, but for this layer the magnetic moment is too small to make a firm statement. An even larger increase of the Curie temperature upon lowering the substrate temperature during growth was observed for the case of e-beam evaporated EuS on GaAs [92, 94], where it is explained by the extra carriers that are present due to the nonideal growth of EuS at low temperatures.$^2$

For the sample shown in figures 4.8 and 4.9 a large portion of the expected magnetic moment ($7\mu_B$/atom) appears to be absent. The magnetic moment of the EuS layers will be discussed extensively later in this chapter. In conclusion, although the improvement is not as pronounced as for the Eu$^{2+}$/Eu$^{3+}$ ratio in the XPS spectra, also the magnetic moment of EuS layers increases with the growth temperature. The “best” EuS is grown at higher substrate temperatures (200-400°C).

$^2$This increase in Curie temperature should not be confused with the increase observed by Stachow-Wójcik et al. [90] that is due to contraction of the EuS lattice resulting from strain from the KCl substrate.
Figure 4.9: Temperature dependence of the magnetic moment of EuS upon cooling through the Curie temperature at a fixed field of 5 mT for samples grown at various temperatures. The Curie temperature gradually increased from 15.3 K for a growth temperature of 400°C to 16.8 K for growth at 100°C. The magnetic moment for the EuS layer grown at 50°C was too small to accurately determine the Curie temperature, that appears to be around 25 K.

Figure 4.10: Hysteresis loop of EuS in Si/SiO$_x$/PbS(40Å)/EuS(60Å)/PbS(10Å) at a temperature of 5 K (open circles). The sample was grown at 200°C and annealed afterwards for one hour at 430°C. For comparison also the hysteresis curve of an unannealed sample (closed squares) is given.
The XPS results on the effect of annealing (figure 4.6) showed an improvement of the chemical quality of the EuS layer after an anneal treatment. As a check whether annealing is really feasible, also the effect of annealing on the magnetic properties of the EuS layers was investigated. Figure 4.10 shows the results of such an investigation. The magnetic moment of an annealed EuS layer is indeed higher than that of a comparable layer that was not annealed. However, the change is not as pronounced as what could be anticipated from the XPS spectra (a 16% higher magnetic moment, compared to a 32% increase of the Eu$^{2+}$ intensity with respect to the total XPS intensity).

Also the effect of the neighboring layers on the magnetic properties of EuS was investigated, since realistic devices require the compatibility of EuS with a metallic electrode. A few representative layer sequences are shown in figure 4.11. In contrast to what is expected from the XPS spectra, the magnetic moment is largest for samples grown directly on the Si/SiO$_x$ substrate, without the addition of an extra PbS layer. This discrepancy can be explained if interdiffusion between the PbS and EuS layers takes place. Interdiffusion does not necessarily change the Eu charge state, and therefore does not strongly affect the XPS spectra, but it decreases the remanent magnetic moment of the structure, as Pb$_x$Eu$_{1-x}$S is not ferromagnetic above a certain value of $x$.

The addition of metallic underlayers reduces the magnetic moment of the EuS more than the addition of PbS. This can again be seen as a sign of interdiffusion. Whereas interdiffusion of EuS and PbS “dilutes” the EuS (since Pb$^{2+}$ and Eu$^{2+}$ are iso-electric) and therefore reduces the magnetic moment by reducing the exchange between Eu$^{2+}$ ions, interdiffusion of EuS and metallic layers can change the complete electron configuration of the Eu$^{2+}$ by bonding of the metal to the EuS. From figure 4.11 it can also be concluded that, at least for Al, the magnetic moment of the EuS layer can be partially restored by the addition of a thin layer of PbS at the metal - EuS interface, as the XPS data already suggested. The recovery of the EuS magnetic moment can in principle be due to two causes. Either the PbS provides a better diffusion barrier for Al than EuS, or the presence of the Al layer affects only the part (first few nm’s) of the neighboring semiconductor that is closest to the interface, the region where the EuS was replaced with PbS. Summarizing, it is thus possible to use an Al bottom electrode in combination with a EuS spin filter, although a thin PbS spacer layer may be necessary.

In this chapter the feasibility of magnetoresistance devices based on a spin filter combined with a ferromagnetic counterelectrode is studied. The possibility of using a ferromagnetic top electrode was already demonstrated by LeClair et al. [5], as discussed in the introduction of this chapter. However, since the spin filter layer is usually rather rough, as will become clear later on in this chapter, the interface of the top electrode next to the spin filter will also be rough, which might locally lead to a poorly defined magnetic structure. Here, the possibility of having a ferromagnetic bottom electrode is investigated. As a first example
of a ferromagnetic electrode Co is chosen. In order to be able to vary the relative magnetic alignment of Co and EuS they should have separate magnetic switching fields. Special care has thus to be taken that the Co and EuS magnetic switching fields do not coincide. A well-established standard approach of modifying the Co switching field is to grow a so-called artificial antiferromagnet, a multilayer of two magnetic layers separated by a thin nonmagnetic layer [78, 97]. More specifically, two Co layers that are separated by a thin ruthenium (Ru) layer, are antiferromagnetically coupled. In this configuration the two Co layers switch together at small fields keeping an antiferromagnetic alignment. At larger fields the thinnest layer switches from an antiparallel to a parallel orientation with respect to the thicker one. This way it should be ensured that the thinner layer switches at a larger field than the EuS. The practical sample structure is Ru(40 Å)/Co(120 Å)/Ru(6 Å)/Co(40 Å)/EuS(60 Å)/PbS(10 Å) on a Si/SiO$_x$ substrate. Since usually no direct strong ferromagnetic coupling between EuS and a neighboring ferromagnetic metal is observed (see for instance the measurements by LeClair et al. [5] or the data shown in the next sections of this chapter),

Figure 4.11: Hysteresis curves (T = 5 K) for 60 Å thick EuS layers grown on different underlayers. The EuS layers were grown at 200°C and annealed afterwards at 400°C. The respective sample structures are (on top of Si/SiO$_x$ substrates): EuS/PbS, EuS, PbS/EuS/PbS, Ru/Al/PbS/EuS/PbS, Ru/Al/EuS/PbS, and Ru/Co/Ru/Co/EuS/PbS. In the figure the layer on which the EuS is grown is always indicated.
we grew the EuS layer directly on top of the Co without a nonmagnetic spacer layer. The hysteresis loop of this sample is shown in figure 4.11. From this curve it cannot be concluded that more than one magnetic switch is present in the hysteresis curve. The only clear magnetic switch is observed at 10 mT, although this might actually be consisting of two steps. At fields larger than 30 mT no additional steps in magnetization are observed. Besides that there is only one obvious magnetic switch visible, while three magnetic switches are expected, as mentioned above, also an amount of magnetic moment is missing that cannot be neglected. Since in this sample two ferromagnetic materials are present, the magnetic moment is given in $\mu_{\text{mAm}}^2$, instead of in Bohr magnetons per Eu atom. For this sample a Eu magnetic moment of 0.35 $\mu_{\text{mAm}}^2$ and a Co moment of 1.15 $\mu_{\text{mAm}}^2$ are expected. However, in total only 1.0 $\mu_{\text{mAm}}^2$ is observed, which suggests (chemical) interaction between atoms from the various magnetic layers.

In contrast to what is the case for Al underlayers, the addition of PbS (or Al-PbS) at the Co/EuS interface does not improve the magnetic properties. The hysteresis curves of such samples (not shown here) show a loss of moment that is comparable to that for samples with EuS directly on top of Co. For this reason Co is excluded as the bottom electrode with a EuS barrier. If a magnetic bottom electrode is desired either another ferromagnetic material for the electrode or another spacer between Co and EuS has to be found.

In this section SQUID and XPS measurements have been compared at several occasions. The magnetic moment of EuS layers in EuS/PbS/EuS grown at various temperatures is plotted in figure 4.12 as a function of the Eu$^{2+}$ 3d$_{5/2}$ fraction of the sum of the Eu$^{2+}$ and Eu$^{3+}$ 3d$_{5/2}$ peaks in the XPS spectrum, after substraction of the Shirley background from the XPS spectrum. For this layer thickness the EuS becomes magnetic when the fraction of Eu$^{2+}$ increases from 30 and 40% of all Eu atoms. A further increase of the amount of Eu$^{2+}$ ions leads only to a slow increase in magnetic moment indicating that the additional Eu$^{2+}$ is not completely magnetized at the applied field of 30 mT, which is possibly due to magnetization of EuS at the interfaces that is diluted with PbS.

To conclude, for spin filter tunnel junctions best EuS layers are obtained by growing at 200°C and annealing afterwards at 400°C. The addition of a metallic bottom electrode always has a negative influence on the chemical quality as well as on the magnetic moment of the EuS (spin filter) layer. On the other hand, at least for Al, the addition of a thin layer of PbS at the Al-EuS interface suppresses this negative influence almost completely. Finally, it has to be mentioned that none of the EuS layers shown above approaches the bulk EuS magnetic moment of 7 $\mu_B$ per atom. At 5 K and 30 mT, the 60 Å thick EuS layer grown directly on the Si/SiO$_x$ substrate has the highest magnetic moment, reaching up to 5.9 $\mu_B$.

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3To be more precise, the transition occurs when 40% of the XPS intensity originates from Eu$^{2+}$. XPS is more sensitive to Eu close to the sample surface than to Eu that is located deeper in the sample.
Figure 4.12: Magnetic moment of several PbS(40Å)/EuS(60Å)/PbS(10Å) samples at 30 mT measured by SQUID magnetometry as a function of the Eu$^{2+}$ peak fraction of the total of Eu$^{2+}$ and Eu$^{3+}$ 3d$_{5/2}$ peaks in the XPS spectrum after substraction of the Shirley background. The Eu$^{2+}$ fraction was adjusted by changing the growth temperature. The uncertainty in the Eu$^{2+}$ fraction is around 10%. The dashed line is a guide to the eye.

per europium atom, although it is not yet completely saturated. This moment is 84% of the bulk value. The slow saturation of the EuS is comparable to that of MBE-grown EuS thin films [92, 98]. At the end of this chapter the saturation magnetic moment of the EuS layers will be discussed in more detail.

4.4 Magnetoresistance of Al/EuS/Gd spin filter tunnel junctions

In order to measure a magnetoresistance based on EuS spin filters devices were prepared with a layer of EuS as a tunnel barrier between two crossed metallic stripe electrodes. Although many junctions were grown (>300) with a great variety of layer sequences, only a few samples did show a hysteretic magnetoresistance effect. This section will describe the results that were obtained on sample structures that were based on EuS with an Al bottom electrode and a Gd top electrode. The choice for Al as the bottom electrode was based on the discussion in section 4.3. Moreover, the working spin filter tunnel junction by LeClair et al. [5] was based on an Al bottom electrode. The discussion in this section is limited to two specific sample structures. Both rely on a Gd top electrode com-
bined with the Al bottom electrode. For one of the structures the EuS is grown at 400°C and sandwiched between two thin PbS separation layers, resulting in a Ta/Al/PbS/EuS/PbS/Gd/Al system (system A). For the other no PbS is used and the EuS layer is grown at 200°C and afterwards annealed at 430°C, leading to Ta/Al/EuS/Gd/Al (system B). The next section will give an overview of alternative device structures, where no clean hysteretic magnetoresistance was observed.

Devices with a EuS barrier grown at 400°C (system A) showed low resistances (<100 Ω at a junction area of 0.2 mm²) for barriers below 100 Å. For thicker barriers the junction resistance abruptly jumped to values above 10⁵ Ω (resistance-area product \(R \times A > 2 \times 10^{-2} \text{Ωm}^2\)). The initial low resistance is indicative for pinholes in the barrier layer. The barrier thickness at which the resistance abruptly increases corresponds then to the thickness at which the majority of the pinholes is closed. The high value of this thickness can be regarded as a sign of a high barrier roughness, as mentioned already in section 4.3. In contrast, the barriers grown at 200°C (system B) show this resistance jump at lower thicknesses of 60-80 Å, suggesting a lower roughness. More specifically, without annealing the resistance is typically 10-100 kΩ for layers that are 100 Å thick. After annealing at 430°C the resistances rise to the order of 100 MΩ at 5 K. This corresponds to resistance-area products \(R \times A\) of the order of 20 Ωm² for annealed EuS layers of 100 Å. The resistivity of EuS (exceeding 10⁹ Ωm) was too high for a direct in-plane Hall and resistivity measurement. Also junctions were grown with only a PbS (1000 Å) layer, and no EuS (Al/PbS/Ru junctions), to exclude that the high resistance is due to the PbS instead of the EuS. These showed resistances below 100 Ω at 5 K, indicating that the high resistance is only due to the EuS barrier layer.

Figure 4.13 shows the magnetoresistance curve of a Al/PbS/EuS/PbS/Gd device (system A) with a 120 Å EuS barrier layer grown at 400°C. The PbS layers were added as a diffusion barrier between the Al electrode and the EuS spin filter and as a spacer to promote independent switching of EuS and Gd. This junction showed a hysteretic magnetoresistance effect with sharp switching fields. Before discussing the actual magnetoresistance curve it is useful to have a look at the current-voltage characteristic given in the inset. Clearly, the current through the EuS layer is nonlinear with the applied voltage, which is characteristic for tunnelling processes. Later on, the current-voltage characteristics of an Al/EuS/Gd will be discussed in more detail.

The magnetoresistance curve can be explained as follows. When decreasing the magnetic field from positive high fields, the junction resistance rises abruptly at a negative field of a few mT suggesting a change in magnetization orientation of the magnetic layers from parallel to antiparallel. Later, at a negative field

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4The low resistivity of PbS is due to the low gap of 0.4 eV and the location in the conduction band of energy levels of electrically active vacancies, see chapter 1 and Dornhaus et al. [29]
Figure 4.13: Resistance of an Al/PbS/EuS/PbS/Gd junction (system A) as a function of an external magnetic field at a current of 0.1 µA at $T = 5$ K. EuS was grown at 400°C and was not annealed. Gd was added as the second ferromagnetic layer. The inset shows the $I - V$ curve for the same junction at 5 K.

of 0.8 T, their magnetizations align in parallel again. As expected based on section 4.1, the antiparallel state has the highest resistance. The switching at low fields can be ascribed to the EuS layer (see the SQUID data in the previous section), and the one at 0.8 T to the Gd. The switching is better defined than was observed earlier by LeClair et al., although the value of the Gd switching field is still remarkably high (the switching field as measured by SQUID is typically 0.08 T). The high switching field of Gd might be indicative of a high roughness of the underlying EuS, that will be discussed later on in this chapter. If deep valleys or thin spots are present in the EuS layer, they will be filled with PbS and Gd, providing a current channel through the junction with a lower resistance. The effective switching field that is related to the transport is not the switching field in the interior of the Gd layer, but the switching field of the Gd in the valley. The presence of a clear transition in the resistance related to the magnetization orientation of both layers (similar to a spin valve device) indicates that EuS is acting as a spin filter layer. We believe that the low value of the magnetoresistance of 1.4% is due to the low value of the PbS resistance compared to the one of the barrier layer (see chapter 5 and reference [4]). Because of its narrow band gap and the location of the Fermi level close to its conduction band, PbS can have a small amount of electron states available, such that at least part of the tunnel current is from or into the PbS layers, instead of directly from the Gd through the semiconductors to the Al. The observed linear background in the magnetoresistance could be related to the modulation of the barrier conductance.
by the Zeeman effect. Although much smaller than the exchange splitting, the
Zeeman energy modifies the absolute height of the tunnel barrier for each spin
subband, to which the transmission probability of the barrier layer is extremely
sensitive. This way the spin filter efficiency of the EuS is changed, leading to
a different resistance in combination with the ferromagnetic Gd electrode. The
positive slope (for positive fields) is not completely understood, but it actually
suggests that the field decreases the splitting of the conduction band, i.e. that
the Zeeman shift of the bottom of the conduction band is opposite to the shift
due to exchange with the EuS 4f magnetic moment.

![Graph](image)

**Figure 4.14:** Magnetoresistance of an Al(100 Å)/EuS(100 Å)/
Gd(200 Å) spin filter tunnel junction at a bias voltage of 2.4 mV
at a temperature of 5 K. A magnetoresistance of 12% is observed
($R_0 = 80 \, \text{k}\Omega$). The grey line is the resistance measured by sweeping
the field in the positive direction; the black line by sweeping in
the negative direction.

The other system of this type that is discussed here is the Al/EuS/Gd sys-
tem, without any spacer layers (system B). This is the same system as the one
described by LeClair *et al.* [5]. In the samples mentioned here the EuS was always
(sputter-) grown at 200°C followed by an anneal treatment for 1 hour at 430°C, in
accordance with the results described in the previous section. Figure 4.14 shows
a magnetoresistance curve of a device with this layer sequence, measured at 5 K.
A magnetoresistance effect of 12% is visible, with sharp switches. These are
associated with the transition of the two magnetic layers between a state of parallel
orientation and one of antiparallel orientation. For comparison, the hysteresis
curve of a similar sample, in which the electrode strips are replaced with layers
of the same material, that cover the complete sample, is given in figure 4.15. The
curve at 5 K shows two magnetic switching fields, one abrupt switch around zero.
field, the other more gradual at fields between 50 mT and 100 mT. Since in the
30 K hysteresis loop (above the Curie temperature of EuS) only the latter is still
visible, the Gd is associated with the switch at 50-100 mT and the switch at small
fields is attributed to EuS. These switching fields coincide reasonably well with
those in the magnetoresistance data, indicating that in this case the transition
at small fields is due to switching of the EuS and the one at higher fields can
indeed be attributed to Gd. As to the magnitude of the magnetic moment, from
figure 4.15 it appears that a significant part of the magnetic moment is missing,
since the moment of EuS should be 0.60 \( \mu \text{Am}^2 \) and that of Gd 1.9 \( \mu \text{Am}^2 \). In
section 4.6 a detailed study of the magnetic moment of both the EuS and the Gd
layer will be presented.

\[ \mu (\mu \text{Am}^2) \]

\[ \mu_0 H (\text{mT}) \]

**Figure 4.15:** Hysteresis loop of an Al(100Å)/EuS(103Å)/Gd(200Å)
sample, measured both below (5 K) and above (30 K) the Curie
temperature of EuS. Two switches are observed: a sharp one at low
fields, attributed to EuS, and a more gradual one at higher fields,
assigned to Gd.

The current - voltage curve of an Al/EuS/Gd spin filter tunnel junction is
depicted in figure 4.16. The current - voltage behavior is clearly nonlinear, a sign
of tunneling as the transport mechanism through the junction. However, it should
be mentioned that also a Schottky barrier and even conduction through pinholes
can lead to a nonlinear current-voltage curve [99]. The curve was fitted with
the equation derived by Brinkman *et al.* [43] for tunnel junctions with unequal
electrodes, equation 2.14. Fits for the low and the high voltage part of figure 4.16
give slightly different values for the fit parameters, indicating that the Brinkman
fit does not describe the current voltage behavior perfectly. This is probably due
to the relatively high barrier asymmetry. Both the effective barrier thickness \( d \)
Chapter 4. MR based on a EuS spin filter and a ferromagnetic electrode

![Figure 4.16: Current-voltage curve of an Al(150Å)/EuS(103Å)/Gd(200Å) spin filter tunnel junction at a temperature of 5 K without an external field. The data have been fitted with the theoretical curve described by Brinkman et al. [43], equation 2.14, in the range from -0.4 V to 0.4 V.](image)

as well as the effective barrier height $\varphi$ and its asymmetry $\Delta \varphi$ are obtained from the fit. The effective barrier thickness is much lower than its nominal thickness. This can be linked to the aforementioned roughness of the EuS, since the current will always follow a path through the thinnest part of the barrier, which can be significantly lower than the average barrier thickness for rough layers. For the same reason the roughness reduces the effective area of the junction. However, for the fit the nominal junction area was used, so the effective area itself was not obtained from the fit. The tunnel current depends much stronger on the barrier height and thickness than on the junction surface, and therefore a small change in barrier height or thickness would already cause a large deviation in the fitted junction area. On the other hand, the fitted values obtained for the barrier height and thickness are still upper boundaries and the real barrier height and thickness can be slightly lower, resulting from a smaller effective junction area. At the end of this chapter, the EuS roughness will be described in more detail. The effective barrier height of 0.71 eV is somewhat lower than the energy level of the bottom of the conduction band with respect to the Fermi energy of bulk EuS [18] if the spin splitting of the conduction band is taken into account, see chapter 2. The asymmetry in the barrier of 0.62 eV is in line with the difference in workfunction between the Al (4.2 eV) and Gd (2.9 eV) electrode [100]. It is also possible that the Al surface oxidizes before growth of the EuS barrier and thus forms a thin layer of $\text{Al}_2\text{O}_3$ at the Al - EuS interface. That would also cause an asymmetry of the barrier.
Another hallmark feature that allows identification of a spin filter tunnel barrier is a decrease of its tunneling resistance below the Curie temperature. The transmission through a tunnel barrier was given in equation 2.12. As can immediately be noticed the transmission strongly depends on the barrier height. The resistance of a tunnel junction is inversely proportional to the transmission of the barrier. Since the barrier height depends on the exchange splitting of the EuS conduction band and the exchange splitting is temperature dependent, also the device resistance depends on temperature. More specifically, below the Curie temperature of EuS the barrier height decreases for electrons of one spin orientation leading to a lower resistance. The temperature dependence of a Al/EuS/Gd device is given in figure 4.17. Indeed a “resistance drop” is observed around the Curie temperature of EuS. The decrease of the resistance above 50 K is attributed to the existence of defect states in the barrier above the Fermi level. As the thermal energy of the electrons increases, they can gain enough energy to hop between those defects, creating a more effective transport mechanism than tunneling. As a result the EuS is only a good tunnel barrier at low temperatures. In an alternative explanation Wrotek et al. [101] attributed the decrease of the junction resistance with temperature to a lowering of the EuS barrier height. However, the decrease in resistance that is observed here (for many of our samples the resistance at room temperature is several orders of magnitude lower than at cryogenic temperatures) is too large to be only due to a decrease of the EuS barrier height.

It is reasonable to assume that the exchange splitting is proportional to the EuS magnetization, since both the magnetization and the exchange splitting originate from alignment of the local Eu$^{2+}$ moments. With this assumption the junction resistance, that is inversely proportional to the barrier transmission, see relation 2.18, can also be written as a function of the EuS moment:

$$ R \simeq e^{2d} \sqrt{\frac{2m}{\hbar^2} (\phi - \frac{1}{2} \frac{M}{M_{\text{sat}}} \Delta)}. \quad (4.8) $$

Here, $M$ and $M_{\text{sat}}$ are the EuS magnetization and its saturation value, respectively, and $\Delta$ is the zero temperature exchange splitting of the conduction band. Starting from a measurement of the magnetization versus temperature, like the measurement shown in figure 4.9, optimal values of $\Delta$ and $d$ can be determined by simulating the resistance, if for $\phi$ the literature value of 1.6 eV for the EuS barrier height is substituted. We defined as the best simulation the one that correctly describes the values of the resistance of the junction above the Curie temperature ($30-40$ K) and well below the EuS Curie temperature. The result is plotted as the grey line in figure 4.17. The curve resembles the qualitative behavior of the resistance with temperature for an exchange splitting of 0.32 eV, and a barrier thickness of 2.5 nm, indicating that tunneling through a magnetic barrier is indeed the transport mechanism. Again the effective barrier appears to be thinner than what was originally grown (8.0 nm), pointing at a high barrier
roughness. The decrease of the resistance occurs already at a higher temperature than the onset of the magnetization, which can be inferred from the horizontal distance between the calculated curve, that is based on the exchange splitting and magnetization, and the measured curve. This can be explained by the fact that tunneling mainly takes place through the thinnest spots in the barrier, which do not necessarily possess the same magnetic properties as the thicker parts of the barrier.

![Graph](image)

**Figure 4.17:** Temperature dependence of the resistance of an Al(100Å)/EuS(80Å)/Gd(200Å) spin filter tunnel junction, measured at increasing temperatures in a magnetic field of 0.8 T to ensure full magnetization of the EuS layer. The grey line is a plot of the resistance according to equation 4.8 in which the exchange splitting of the EuS tunnel barrier height is taken proportional to its magnetic moment. The moment was measured in a layered structure in which the Gd was replaced with (nonmagnetic) Ta.

Finally, from the foregoing results it appears to be possible to produce spin filter tunnel junctions that are based on EuS layers. However, as mentioned before the reproducibility in fabricating these tunnel junctions is poor. The data presented in this section are selected from a few dozen of batches of 24 junctions each. In total only a few of those exhibit any spin filtering behavior and even less show a magnetoresistance effect (order of 10 junctions). This can, as suggested before, be attributed to the roughness of the barrier layer. Moreover, a rough interface between the ferromagnetic electrode and the spin filter might also lead to a poorly defined magnetic structure at the interface where both the magnetic electrode and the spin filter are present next to each other. In the last section of this chapter some attention will be devoted to the layer roughness. A device
having the bottom electrode as the magnetic electrode would be preferential, since it should contain a much smoother interface between the ferromagnetic electrode with a more transparent local magnetic structure than a device with a magnetic top electrode. Such structures will be investigated in the next section.

In conclusion, EuS spin filter tunnel junctions can in principle be sputtered. However, the reliability of Al/(PbS)/EuS/(PbS)/Gd devices is still poor. A likely cause is the roughness of the barrier layer, leading to unpredictable current paths and potentially to a locally badly defined magnetic structure. The role of imperfections in the growth of the ferromagnetic top electrode on the barrier is not clear. Therefore, it makes sense to also check the feasibility of samples with other layer sequences, which will be discussed in the next section.

4.5 Other sample layouts for spin filter devices

While the previous section was limited to devices based on EuS combined with Gd as the ferromagnetic electrode, this section addresses other systems that potentially exhibit a spin-filter magnetoresistance effect. Of course, in principle many sample layer sequences are possible, although in practice many of them suffer from incompatibility of materials, too large barrier roughness, etc.

Table 4.1 gives a list of most layer sequences that were tested as possible magnetoresistance devices. In addition, the results for these samples are given or, alternatively, the reason why they failed. For simplicity, seed layers, usually Ta, and capping layers, mainly Al, are not mentioned. Generally, the first check was whether at least the magnetic properties throughout the sample are as intended. Systems that do not exhibit a magnetic moment from both a ferromagnetic spin filter layer and a ferromagnetic electrode (because of intermixing or reacting with other layers for instance) are immediately excluded as suitable spin filter systems. The second step is to check the electrical behavior of a corresponding tunnel junction structure. The electrical resistance of the electrodes was measured as well as the resistance of the tunnel barrier. Many systems did not consist of an insulating tunnel barrier and two conducting electrodes, and these are therefore not taken into further consideration.

The two systems based on EuS as the spin filter and Gd as the ferromagnetic electrode that are labeled with “MR” were already treated in the previous section. Of all other layer sequences mentioned in table 4.1 CoFe/Al₂O₃/EuS/Ta, based on either Co or CoFe and with or without thin Al or Gd layers, appears to be the most promising. The rest of this section will deal with this system only. Although the results will be rather disappointing, they serve as an example of the work that was done to investigate spin filtering with EuS in other systems. This particular layer sequence shows at least the required magnetic behavior. Moreover, for this sample the bottom electrode is the magnetic electrode, probably leading to a smoother interface between the magnetic electrode and the spin filter, which
Table 4.1: Overview of the EuS spin filter systems we investigated. Also the results with these systems or, alternatively, the main reasons of failure are included. Buffer and capping layers are not mentioned; usually Ta is used as a seed layer and Al is used as a cap.

<table>
<thead>
<tr>
<th>System</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/EuS/Gd</td>
<td>MR</td>
</tr>
<tr>
<td>Al/EuS/Co</td>
<td>EuS not magnetic</td>
</tr>
<tr>
<td>Gd/EuS/Al</td>
<td>Gd not magnetic</td>
</tr>
<tr>
<td>Al/PbS/EuS/PbS/Gd</td>
<td>MR</td>
</tr>
<tr>
<td>Co/PbS/EuS/PbS</td>
<td>only 1 magnetic component</td>
</tr>
<tr>
<td>Co/Al/PbS/EuS/PbS</td>
<td>only 1 magnetic component</td>
</tr>
<tr>
<td>Co$<em>{80}$Fe$</em>{20}$/Al/EuS/Ta</td>
<td>only 1 magnetic component</td>
</tr>
<tr>
<td>Gd/Al$_2$O$_3$/EuS/Al</td>
<td>Gd not magnetic</td>
</tr>
<tr>
<td>Co/Al$_2$O$_3$/EuS/Al</td>
<td>depends on Al$_2$O$_3$ thickness and oxidation</td>
</tr>
<tr>
<td>Co$<em>{80}$Fe$</em>{20}$/Al$_2$O$_3$/EuS/Ta</td>
<td>depends on Al$_2$O$_3$ thickness and oxidation</td>
</tr>
<tr>
<td>Co$<em>{80}$Fe$</em>{20}$/Al$_2$O$_3$/Al($\delta$)/EuS/Ta</td>
<td>no MR</td>
</tr>
<tr>
<td>Co$<em>{80}$Fe$</em>{20}$/Al$_2$O$_3$/EuS/Gd($\delta$)/Ta</td>
<td>2 switches, MR?</td>
</tr>
<tr>
<td>Co$<em>{80}$Fe$</em>{20}$/MgO/EuS/Gd</td>
<td>no MR</td>
</tr>
<tr>
<td>GaAs//EuS/Gd/Al</td>
<td>no EuS barrier observed electrically</td>
</tr>
</tbody>
</table>

provides a better defined structure. However, in section 4.3 it was concluded that a Co ferromagnetic bottom electrode had a negative influence on the EuS spin filter. For this reason the Al$_2$O$_3$ layer was added. It will be shown that for this layer sequence at least the magnetism of the layers is well defined. For these sample structures the bottom part, including a Ta seed layer, exactly resembles the sample structure of an “ordinary” magnetic tunnel junction, see for instance the report by LeClair [39]. It is thus possible to take advantage of the expertise in the field of magnetic tunnel junction research [102].

The hybrid Al$_2$O$_3$/EuS barrier requires some special attention. From the resistance of a tunnel barrier of finite height, equation 2.12, it can be inferred that the nonmagnetic part of the barrier enhances the total resistance of the barrier, but that it does not change the spin filtering efficiency of the barrier, as it reduces the transmission of spin-up and spin-down electrons equally. In chapter 5 the effect of any nonmagnetic part of the tunnel barrier is explained in more detail.

The hysteresis curve of a Ta/CoFe/Al$_2$O$_3$/EuS/Al sample is plotted in figure 4.18. Two different switching fields are visible, that can be assigned to the two ferromagnetic layers, in clear contrast to what was observed in section 4.3 for samples containing EuS layers directly grown on Co where only one clear magnetic switch was visible. Apparently, the Al$_2$O$_3$ layer forms a diffusion barrier between the two layers, and magnetically separates the CoFe and the EuS.
The hysteresis curve above the Curie temperature of EuS shows a very small coercivity for the remaining CoFe. The magnetic component in the 5 K hysteresis curve with the smallest coercive field is therefore associated with the CoFe layer, the other magnetic component with the EuS layer. The spin filter and the ferromagnetic counterelectrode thus form two independently switching magnetic layers, and from a magnetic point of view this sample structure appears to meet the requirements to show magnetoresistance.

**Figure 4.18:** Hysteresis curve of a Ta(93Å)/CoFe(100Å)/Al₂O₃ (32Å)/EuS(100Å)/Al(30Å) sample at temperatures of 5 K and 30 K, below and above the Curie temperature of EuS, respectively.

Next, the electrical properties for CoFe/Al₂O₃/EuS samples are to be discussed. Several batches of this type were grown, but most of them did not show any magnetoresistive effect. The best result was obtained with a CoFe/Al₂O₃/EuS/Gd/Al sample, in which three ferromagnetic layers are present, although the Gd was initially added only as a buffer layer between the EuS and the Al. The resistance of this device as a function of the applied magnetic field is shown in figure 4.19. Clearly, the magnetoresistance effect is only small, with the largest resistance difference being only 2%. For this small magnetoresistance it has to be checked whether the effect could be explained by means of the anisotropic magnetoresistance effect, AMR, in the ferromagnetic electrodes. AMR is the resistance change of a ferromagnet dependent on the angle between the current and the magnetization of the ferromagnet [103]. This effect is at low temperatures typically a few percent of the resistance of the ferromagnet. However, the resistance of the (ferromagnetic) electrodes is much lower than the junction resistance $R_0$ of 260 kΩ, excluding AMR as the cause of the observed magnetoresistance effect. Despite the small magnetoresistance, it is interesting to check
Figure 4.19: Resistance as a function of magnetic field for a CoFe(100Å)/Al₂O₃(40Å)/EuS(100Å)/Gd(200Å)/Al spin filter tunnel junction, measured at a bias voltage of 4 mV and a temperature of 5 K. The absolute resistance of this junction is 260 kΩ. The lines are guides to the eye that only accentuate features of the curve that show up both for increasing as well as decreasing fields.

whether the jumps in the resistance could actually be related to switching of the three ferromagnetic layers. The hysteresis curves of EuS with one ferromagnetic electrode, figures 4.15 and 4.18, suggest that the CoFe switches first, followed by the EuS, and finally the Gd. The fact that both CoFe and EuS appear to switch their magnetizations just before the field crosses zero might in principle be due to (antiferromagnetic) interactions with the Gd layer, causing the magnetic switching fields to shift. When following the magnetoresistance curve in the positive field direction, at large negative fields all three magnetic layers are oriented in parallel, leading to a constant resistance in this regime. After the first jump the orientation of the CoFe has changed, and has become antiparallel to that of EuS and Gd; the resistance of the device has risen accordingly to 1.005 times the starting value. Next, the EuS switches and becomes oriented parallel to the CoFe again, leading to a lower resistance (0.99 × R₀). Finally, upon the switch of Gd the resistance reassumes its original value. However, even though the effects are small, the parallel states at large fields should correspond to the lowest resistances. More specifically, these data suggest that an antiparallel orientation of EuS and Gd leads to a lower resistance than a parallel one, which is in contradiction with earlier results, see section 4.4 and LeClair et al. [5]. Although an explanation based on speculations about imperfections of the interfaces, leading to modified spin polarizations and a smaller magnetoresistance effect, would be possible, it is clear that obtaining a reproducible magnetoresistance device based
on this sample structure is not straightforward (also taking into account that this is the only junction showing any magnetoresistance).

Resuming, alternative sample layouts for EuS spin filter tunnel junctions are in principle possible. However, no other single ferromagnetic electrode than Gd has shown any magnetoresistance in combination with a EuS barrier. Improvement with respect to the EuS/Gd devices described in section 4.4 should thus be obtained by either improving these two layers or by changing to another spin filter material. One of the problems regarding the EuS/Gd system is that its magnetic properties have not yet been understood. The next two sections of this chapter focus on the (absence of a strong ferromagnetic) coupling between the spin filter and the ferromagnetic electrode. Apart from the fact that such a coupling is of interest in itself, a study of magnetic properties can also point out what part of the sample should be improved for the production of a robust spin filter magnetoresistance device.

4.6 Magnetic moment of electrode and barrier layers

In the previous sections the electrical behavior of Al/EuS/Gd spin filter tunnel junctions was investigated without paying too much attention to the magnetic behavior of the individual layers. However, considering the fact that the barrier and one of the electrodes are both ferromagnetic and in direct contact, one would intuitively expect a strong magnetic coupling between the two resulting from direct exchange interactions at the interface. In contrast to this expectation, both the magnetic and electric measurements presented in the previous sections reveal a separate switching behavior of the ferromagnetic layers. This section (4.6) and the following one (4.7) will describe the development of the magnetic moment as a function of the layer thicknesses and the interlayer coupling between the two ferromagnetic layers, respectively, and will try to explain this behavior in terms of the morphology of the sample, in particular in terms of intermixing and roughness at the EuS/Gd interface.

For a SQUID study of the switching behavior of the two ferromagnetic layers a series of homogeneous multilayers was grown in which Gd was grown directly on top of EuS, for several combinations of thicknesses of the EuS and Gd layers. The EuS/Gd bilayers were grown on oxidized silicon substrates on top of a 20 Å Ta seed layer and a 50 Å Al buffer layer. The complete structure was capped with a 20-25 Å Al layer. With this layer sequence these samples exactly resemble the junctions described in section 4.4. As an example, in figure 4.20 the hysteresis curve of a planar sample with a EuS thickness of 60 Å and a Gd thickness of 80 Å is plotted, analogous to figure 4.15. As a short reminder, two magnetic switches are observed, that are ascribed to the two individual ferromagnetic layers. The
Figure 4.20: Hysteresis loops of a Ta/Al/EuS(60Å)/Gd(80Å)/Al sample grown on an oxidized silicon substrate. The nominal magnetic saturation moments are $349\ \text{nAm}^2$ for the EuS and $812\ \text{nAm}^2$ for the Gd. Both loops below (5 K) and above (30 K) the Curie temperature of EuS are presented.

The magnetic moments of the EuS and Gd layers can be extracted from the hysteresis curve in two ways. One can try to fit the two switches of the magnetic moment in the 5 K curve, as will be explained later on. Alternatively, the magnetic moments of EuS and Gd can be extracted from hysteresis curves above and below the EuS Curie temperature, as will be shown here. We will call this approach “method I”. For both ferromagnetic layers the measured magnetic moment is smaller than the expected moment, which is the most striking for the Gd. From the bulk saturation magnetic moment of Gd of $7.6\ \mu_B/\text{atom}$ a magnetic moment of $812\ \text{nAm}^2$ is expected. As a first approximation the measurement at 30 K, well above the EuS Curie temperature of 16.8 K but well below the one for Gd, is considered to be a measurement of purely the Gd magnetic moment. As figure 4.20 shows, at a field of 0.2 T only $275\ \text{nAm}^2$ is measured. Upon raising the field to 2 T the moment increases unhysteretically to $395\ \text{nAm}^2$, still well below the calculated moment. For the EuS the bulk saturation magnetic moment of $7\ \mu_B/\text{atom}$ translates to an expected moment of $349\ \text{nAm}^2$. Taking the difference in magnetic moment between the 30 K and 5 K measurements to be due to the EuS, the moment measures up to $255\ \text{nAm}^2$ at 0.2 T, and $285\ \text{nAm}^2$ at 2 T. However, one should realize that for sufficiently large fields already some...
magnetic moment is induced in the EuS even above its Curie temperature, such that it is no longer possible to correctly separate the EuS and Gd contributions. According to mean-field theory (\( g \)-factor of 2; spin quantum number \( S \) of 7/2) this induced magnetic moment can already be 20% of the saturation moment for an applied magnetic field of 2 T.\(^5\) Therefore, for this approach (method I) measurements at lower fields have to be used.

For a more detailed study of the magnetic moment one might thus be inclined to try to fit the switches of the magnetic moment at a temperature below the Curie temperature of EuS, since this will in principle provide the saturation magnetic moments. This approach will be referred to as “method II”. In the ideal case one would observe two sharp switching fields that can easily be ascribed to the two ferromagnetic materials. Then the step size at the two switch fields would correspond to the switching of the magnetization of the individual layers, and the magnetic moment of each layer would be half the step size. However, this situation would require the two ferromagnetic layers to switch their magnetizations completely as two single domains. For the polycrystalline samples under investigation more domains will exist and they will have a distribution of switching fields. Moreover, even a single domain can show a non-abrupt change in magnetization. A first approach is to describe the distribution of these switching fields with a Gaussian distribution. Equivalently, the corresponding hysteresis curve can then be described by a sum of error functions, one for each magnetic layer. For the part of the hysteresis curve going from positive to negative magnetic fields a fit with a sum of three error functions is plotted in figure 4.21 for the same sample as is shown in figure 4.20. The reason for the additional third error function is explained below.

Although only two ferromagnetic layers are present, a fit based on the sum of two error functions does not satisfactorily describe the hysteresis curve, i.e. the distribution of switching fields for each layer is not completely Gaussian. More specifically, this fit could not reproduce the slope of the curve away from the switch fields of the two layers. In order to qualitatively describe the full curve at least one extra error function would be needed. An intuitive approach would then be to describe the relatively sharp switch of the magnetic moment of the EuS layer as one error function and the broader switch of the Gd with two error functions. Apart from this intuitive motivation, if the slope at high fields would be completely accounted for by the EuS, its magnetic moment would exceed the theoretical value of 7 \( \mu_B \)/atom. Moreover, the measured curves at 5 K and 30 K, figure 4.20, show a similar slope at higher fields indicating that EuS is not the main contributor. Figure 4.21 shows the results of a fit with three error functions, two to describe the Gd switch and one for the EuS switch. It can be seen that at

\(^5\)In mean-field theory the interactions between all the individual spins in a magnetic material are represented by an average field, working on the individual spins. Mean-field theory provides a description of the development of the magnetization of a material as a function of temperature.
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\[ \mu_{\text{EuS}} = 213 \text{ nAm}^2 \]
\[ \mu_{\text{Gd}} = 443 \text{ nAm}^2 \]

Figure 4.21: Three error function fit of the magnetic moment of a Ta/Al/EuS(60Å)/Gd(80Å)/Al sample measured from the positive to the negative field direction. The fit was performed in the field interval from -2 T to 2 T. The measurement is shown as a solid black line and the fit as a solid grey line. The fit is divided in components associated with EuS (dotted black line) and Gd (dashed grey line), which are both shifted in vertical direction for optimal comparison with the experiment. The magnetic moments of EuS and Gd, as obtained from the fit, are 213 nAm² and 443 nAm², respectively, which can be compared to literature values of 349 nAm² for EuS and 812 nAm² for Gd.

In large positive fields the fit is not perfect. It cannot be excluded that at least part of the broad switching behavior is due to EuS. Therefore, in the determination of the individual moments of the two ferromagnetic layers the saturation moments at 5 K and 30 K will be compared (method I), instead of using the fit with two or three error functions (method II).

As mentioned before, a considerable amount of magnetic moment appears to be absent for both EuS and Gd, as compared to the nominal values. A first test to determine the origin of the missing moment is to check the evolution of the magnetic moments with the layer thicknesses. For a set of samples only varying in Gd thickness the total magnetic moment measured by the SQUID is shown in figure 4.22, as well as the moments of the individual ferromagnetic layers derived from the hysteresis curves at 5 K and 30 K. The magnetic moment in figure 4.22 is measured at 200 mT (instead of 2 T) to prevent that a substantial portion of the measured magnetic moment at 30 K is due to a field-induced magnetic moment of EuS, as mentioned before. The data points at a Gd thickness of 80 Å can be recognized as stemming from the measurement in figure 4.20.
Figure 4.22: Magnetic moments at 200 mT of EuS (triangles), Gd (circles) and their sum (squares) for Ta/Al/EuS(60Å)/Gd/Al samples in which the Gd thickness is varied from 20 Å to 120 Å. Values were obtained by comparing hysteresis curves below (5 K) and above (30 K) the Curie temperature of EuS (16.8 K). The uncertainty in the magnetic moment of the individual layers is about 20 nAm$^2$. The units in the fit are such that the Gd thickness is in Å and the magnetic moment in nAm$^2$.

The first feature that can be noticed in figure 4.22 is that the total moment can be thought of as the sum of a constant and a linearly increasing contribution. Looking at the EuS contribution, this is independent of the amount of Gd put on top within a spread of 20%. Only for the thickest layers the moment measured appears to be a little bit lower. This is in agreement with hysteresis curves of single EuS layers in which saturation is reached at higher fields for the thickest layers. If this is also the case here then the EuS does not have to be completely saturated at the measurement fields.

The Gd moment shows a linear increase with layer thickness, starting at 35 Å. Apparently the first 35 Å of Gd is involved in the formation of interface layers at the EuS-Gd and Gd-Al interfaces and forms a magnetically dead layer. The slope of the linear increase of 6.1 nAm$^2$/Å is approximately 60% of the value calculated from the bulk value of 7.5 μ$_B$/atom. This might possibly be due to oxidation of part of the Gd during the growth, leading to nonmagnetic Gd$_2$O$_3$, although the background pressure was 10$^{-9}$ mbar. Furthermore, Gd and Al tend to form a whole myriad of compounds leading to a smaller amount of pure ferromagnetic Gd [104, 105]. Moreover, after interdiffusion with the Al, Gd might reach the surface of the sample and oxidize there.
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Figure 4.23: Magnetic moments at 200 mT of EuS (triangles), Gd (circles) and their sum (squares) for Ta/Al/EuS/Gd(90 Å)/Al samples in which the thickness of the EuS layer is varied from 40 Å tot 100 Å. Values were obtained from comparing hysteresis curves below (5 K) and above (30 K) the Curie temperature of EuS (16.8 K). The units in the equation of the fit are such that the Gd thickness is in Å and the magnetic moment in nAm².

When the Gd layer thickness is kept constant and the thickness of the EuS is varied a similar behavior is observed, as is depicted in figure 4.23. Now the Gd moment is nearly constant and the EuS moment rises linearly with the layer thickness, as expected. However, the first 15 Å of EuS do not add to the magnetic moment, indicating that, like Gd, also EuS forms a magnetically dead layer. The slope in the EuS moment of 4.5 nAm²/Å corresponds to approximately 80% of the theoretical moment of 7 µB/atom (5.81 nAm²/Å). Overall, both the measured magnetic moments of EuS and Gd are smaller than their expected values. In this analysis it is very important to realize that the value of the magnetic moment at a field of 200 mT is used as the “saturation magnetic moment.” At this field all hysteresis loops (usually measured between -2 T and 2 T) are closed. We expect that all layers that show hysteresis are saturated. However, when going to a much larger field of 2 T a magnetic moment can be observed that is at 5 K about 25% and at 30 K around 50% higher than those from figures 4.22 and 4.23. Hence a large part of the difference between measured and theoretical moments is explained by the difficulty in completely magnetizing the two ferromagnetic layers, especially the Gd. However, also for EuS large fields are often required to completely saturate the material, see for instance chapter 6.

A completely different approach to gain information on the individual mag-
netic moments of EuS and Gd (in contrast to separating the magnetic moments by either method I or II) is to grow samples with only one ferromagnetic layer (either EuS or Gd). This was done for EuS in a series of Ta/Al/EuS/Ta/Al structures and the hysteresis curves are plotted in figure 4.24a. What should immediately be noticed is the (more or less trivial) monotonous increase of the magnetic moment with the EuS thickness. Apart from this, the coercivity of the EuS layers also rises with the layer thickness. Moreover, for the thickest layers a larger field is required to saturate the EuS magnetization along the field, as can be concluded from the steeper slope of the curve at higher fields, that proceeds outside the frame of the graph. As a result, an increasing amount of EuS magnetic moment is not accounted for in a measurement at low fields for these layer thicknesses.

The magnetic moment behaves similarly as a function of temperature as shown in panel b of figure 4.24. Below the Curie temperature of 16.8 K the Eu$^{2+}$ moments start to align and the magnetic moment rises monotonously with temperature in this regime. For the thickest EuS layers the magnetic moment increases slower (with thickness) than for the thinner EuS layers, which is due to the relatively small applied magnetic field of 2 mT and the high fields that are necessary to completely magnetize the EuS, as is also the case for the low-field hysteresis curves. The thinnest EuS layer is barely magnetic with a Curie temperature well below that of bulk EuS.

The magnetic moment of the EuS layers shown in figure 4.24 is plotted in figure 4.25 for higher applied fields of 200 mT and 2 T. For a meaningful comparison with the EuS moments from the EuS/Gd samples first the magnetic moment at a field of 200 mT and at 5 K is considered, although in reality the magnetic moment is still not in saturation at this field. After the initial dead layer of 17.4 Å the magnetic moment increases with 5.6 nAm$^2$/Å, which corresponds to 6.8 $\mu_B$ per Eu ion (the bulk value is 7 $\mu_B$). For the thickest layers the moment increases again slower. This can be ascribed to the fact that for these layers larger fields are needed to align the magnetization along the field direction, and that a measurement at 200 mT shows only part of the magnetic moment. Furthermore, from the full hysteresis loops up to a field of 2 T, it appears that at larger fields the EuS magnetic moment still rises for all layer thicknesses. In figure 4.25 it can be seen that the increase of the magnetic moment with the EuS thickness is slightly faster (7.3 $\mu_B$ per Eu atom) for the 2 T field than for a field of 200 mT. Since the addition of extra EuS increases the amount of EuS that is located away from the interfaces, the higher slope of the 2 T graph indicates that the magnetization in the central part of the EuS layer increases. At 5 K such an increase can indeed be expected from mean-field theory. The magnetically “dead” layer decreases in thickness, although this happens only for large fields - a nonmagnetic layer is still left for the 2 T applied field. The EuS can thus be thought of as consisting of a ferromagnetic layer that is sandwiched between interface layers that can only be magnetized with high enough fields (> 1 T).
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Figure 4.24: Hysteresis curves (a) and temperature dependence of the magnetic moment (b) of EuS layers of 26-156 Å thickness, in steps of 26 Å, in which the moment rises monotonously with thickness. The layer sequence was Ta/Al/EuS/Ta/Al. The hysteresis curves were measured at a temperature of 5 K, the moment as a function of (decreasing) temperature was measured in a field of 2 mT.

Figure 4.25: Magnetic moment at 5 K of EuS layers in Ta/Al/EuS/Ta/Al structures as a function of the EuS thickness for applied fields of 200 mT (black) and 2 T (grey). The lines are linear fits through the first four points for for each applied magnetic field. The dimensions in the equations are such that the layer thickness is always in Å and the magnetic moment in nAm².
Figure 4.26: EuS hysteresis curves at 5 K for (a) EuS/PbS, (b) EuS/Au, and (c) EuS/Ta structures. All structures were grown on Ta/Al and capped with Al. The EuS layers were 60 Å thick, corresponding to an expected moment of 349 nAm$^2$.

When comparing the magnetic moment of EuS in both different sample structures as shown in figures 4.25 and 4.23, Ta/Al/EuS/Ta/Al and Ta/Al/EuS/Gd/Al, it appears that the moment per Ångstrom is higher for the former. This suggests that for the latter a larger field is required to align the EuS magnetization along the field. This could be caused by structural effects, but another explanation could be related to magnetic interactions between EuS and Gd over the dead layer. In any case, from the EuS/Ta sample it appeared that this “dead” layer can be magnetized at large fields ($\gg$ 200 mT). It is thus likely that the increase of the magnetic moment at large fields in the EuS/Gd hysteresis curve shown in figure 4.20 is also partially due to EuS.

Figure 4.26 shows hysteresis curves of EuS covered with various layers, to check whether there is an important influence of the overlayer on the structure of the EuS. The EuS layer that is covered with PbS has the highest magnetic moment; metal-covered EuS has a lower magnetic moment. The fact that the EuS magnetic moment depends on which layer is grown on top of it again corroborates earlier data indicating that the loss of moment takes place at the interface, as this is where the influence of the overlayer is likely to be largest.

Apart from this, the fact that both the EuS and Gd contribute to nonmagnetic dead layers combined with the lack of a strong ferromagnetic coupling also suggests that (part of) this nonmagnetic layer exists at their common interface. If any magnetic coupling is present, this coupling has to occur across this nonmagnetic interface. In the remainder of this chapter the existence and character of the coupling between EuS and Gd will be investigated.
4.7 Interlayer coupling between EuS and Gd

Whereas the interlayer coupling between metallic layers has been studied intensively [49, 53, 54], as was already described in chapter 2, little is known about the coupling between a ferromagnetic metal and a ferromagnetic semiconductor. Rücker et al. [106] studied the interlayer coupling between EuS and Fe, in which case the EuS was grown on top of the Fe. They observed a strong antiferromagnetic coupling below the Curie temperature of EuS. Fumagalli et al. [107] investigated coupling between EuS crystallites and a surrounding Co matrix. Again a strong antiferromagnetic coupling was found. Moreover the EuS Curie temperature was found to increase to over 100 K for certain crystallite concentrations. This increase was explained by a change in the EuS band structure, which can lead to an increase in charge carriers. These can mediate a strong exchange coupling between the EuS crystallites and the Co matrix. However, the coupling between Gd and EuS thin layers is still unknown.

A first indication of coupling between the EuS and the Gd can be observed in figure 4.27 for a Ta/Al/EuS(60Å)/Gd(90Å)/Al sample. In this figure the total magnetic moment of the two layers together is plotted while going down in temperature in a fixed field. At temperatures well above the Curie temperature of EuS only the Gd is visible that should be oriented along the applied field. Then, when cooling through the EuS Curie temperature various things happen, dependent on the magnitude of the applied magnetic field. For sufficiently large fields - 10 mT and 2 mT - the EuS orients along the field direction as is expected. However, for smaller fields - 0.5 mT and 0.2 mT - the EuS magnetic moment develops in the direction opposite to the field direction. In both cases the (larger) Gd magnetic moment remains oriented along the field. The EuS alignment opposite to the field direction is a clear sign of antiferromagnetic interaction between the two ferromagnetic layers.

In order to quantify this antiferromagnetic interaction further and determine the order of magnitude of the coupling constant, a simple Stoner-Wohlfarth model is applied to describe the magnetic energy per surface unit, $E/A$, taking into account only magnetostatic energy and interlayer coupling:

$$ E/A = -\mu_0 H M_{\text{EuS}} t_{\text{EuS}} \cos(\vartheta_{\text{EuS}}) - \mu_0 H M_{\text{Gd}} t_{\text{Gd}} \cos(\vartheta_{\text{Gd}}) - J \cos(\vartheta_{\text{EuS}} - \vartheta_{\text{Gd}}). $$

Here, $M_{\text{EuS}}$ and $M_{\text{Gd}}$, and $t_{\text{EuS}}$ and $t_{\text{Gd}}$ are the magnetization and thickness of the EuS and Gd layers, respectively. $\vartheta_{\text{EuS}}$ and $\vartheta_{\text{Gd}}$ are the angles of the EuS and Gd magnetization with respect to the direction of the field $H$. Note that the exchange coupling energy $J$ is negative if the coupling is antiferromagnetic. Around the Curie temperature of EuS the EuS magnetic moment will, by definition, be smaller than the Gd moment, and therefore the Gd will be completely aligned along the field at this stage. Moreover, for the samples that are discussed in
Figure 4.27: (a) Magnetic moment as a function of temperature for a Ta/Al/EuS(60Å)/Gd(90Å)/Al sample, for various fixed magnetic fields. The temperature was swept from high to low. Panels (b-e) zoom in on the four curves in panel (a) below 50 K. The lines are mean-field simulations of the total magnetic moment of the Gd and EuS layers.
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This chapter the Gd saturation moment is usually larger than that of EuS for all temperatures so it will remain along the field direction. Thus, the angle between the Gd moment and the field direction can be taken as zero ($\theta_{\text{Gd}} = 0$), in which case the energy will only depend on the angle of the magnetization of the EuS. It is then straightforward to conclude from equation 4.9 that the energy is minimal for $\theta_{\text{EuS}} = 0^\circ$ if $\mu_0 H M_{\text{EuS}} t_{\text{EuS}} > -J$ and that it is minimal for $\theta_{\text{EuS}} = 180^\circ$ if $\mu_0 H M_{\text{EuS}} t_{\text{EuS}} < -J$. Since $J$ describes the coupling between $M_{\text{EuS}}$ and $M_{\text{Gd}}$, the coupling energy is divided by the magnetizations of the two layers, to obtain the exchange coupling constant, analogous to the microscopic situation.\(^6\) If the coupling energy is now written as $J = M_{\text{EuS}} M_{\text{Gd}} J_0$, and, as a first-order approximation, $J_0$ is considered to be independent of the layer magnetizations, then

$$\theta_{\text{EuS}} = 180^\circ \quad \text{if } \mu_0 H t_{\text{EuS}}/M_{\text{Gd}} < -J_0 \quad \text{and}$$

$$\theta_{\text{EuS}} = 0^\circ \quad \text{otherwise.}$$

Most of the parameters in this condition can be considered independent of temperature well below the Curie temperature of Gd. The field is kept constant, the EuS thickness is a material parameter, and from figure 4.27 it can be concluded that the Gd magnetization is approximately constant in the temperature range in which EuS becomes magnetic. If the exchange coupling constant $J_0$ is also taken independent of temperature, it immediately follows that upon cooling through its Curie temperature the EuS starts to align either parallel to the field and the Gd magnetization or exactly antiparallel, and that the alignment of the EuS magnetization does not change during further cooling. This is in close agreement with figure 4.27. The only exception occurs in figure 4.27c, where the EuS magnetic moment initially (around the EuS Curie temperature) appears to align antiparallel to the Gd, before it assumes a parallel alignment well below the EuS Curie temperature. So far $M_{\text{Gd}}$ and $J_0$ were assumed to be constant. However, at this field (of 2 mT) the system is already close to the transition between a parallel and an antiparallel alignment and a small change of $M_{\text{Gd}}$ or $J_0$ can change the preferential alignment. At fields that are further away from this transition, see figure 4.27b, d and e, the magnetic alignment of the EuS and the Gd remains indeed constant with temperature.

The order of magnitude of the coupling can now be obtained from figure 4.27. For a field of 0.5 mT the EuS aligns antiparallel to the Gd, whereas at 2 mT the EuS aligns along the field direction, parallel to the magnetization of the Gd. In between these two field values there must be a magnetic field at which the condition for parallel/antiparallel alignment must be exactly an equality, thus providing the following expression for the coupling constant:

$$J_0 = -\mu_0 H t_{\text{EuS}}/M_{\text{Gd}}. \quad (4.10)$$

\(^6\)In a microscopic picture the exchange energy between two spins $\vec{S}_i$ and $\vec{S}_j$ is commonly written as $J_0 \vec{S}_i \cdot \vec{S}_j$, in which $J_0$ is the exchange constant, see also chapter 6.
$J_0$ can be estimated to be $-9 \cdot 10^{-17}$ J/A$^2$ if the field at the transition from antiparallel to parallel alignment is taken to be 1 mT (obtained by interpolation of the change in magnetic moment due to magnetizing the EuS as a function of the applied magnetic field) and the Gd magnetization is 70 kA/m (the Gd volume is $4 \text{ mm} \times 12 \text{ mm} \times 9 \text{ nm}$, the moment is estimated to be 30 nAm$^2$).

Alternatively, it is also possible to determine the coupling energy by comparing the individual graphs in figure 4.27 to similar graphs for simple EuS layers without any Gd, like those in figure 4.24b. The idea behind this approach is that the difference in EuS moment must be due to magnetic interactions with the Gd, represented by an interlayer coupling field. In practice the graphs in figure 4.27 are simulated with curves from mean-field theory, from which the magnetic moments of EuS and Gd are derived. For the 10 mT graph the EuS moment at 0 K is approximately 90 nAm$^2$, resembling that of a curve of a single EuS layer without any Gd in a field of 0.5 mT (not shown). The difference between this effective field of 0.5 mT and the applied field of 10 mT can be considered to be mainly due to coupling, leading to an “interlayer coupling field” $H_{\text{int}}$ of $-9.5$ mT (the effective field is smaller than the applied field). From this field the interlayer coupling constant can be calculated using

$$J_0 = \frac{J}{M_{\text{EuS}}M_{\text{Gd}}} = \frac{\mu_0 H_{\text{int}}M_{\text{EuS}}t_{\text{EuS}}}{M_{\text{EuS}}M_{\text{Gd}}} = \mu_0 H_{\text{int}}t_{\text{EuS}}/M_{\text{Gd}}.$$  \hspace{1cm} (4.11)

If the magnetizations of EuS and Gd are again taken from the mean-field simulations, this method produces a value of the interlayer coupling constant of $-1.7 \cdot 10^{-16}$ J/A$^2$. If the same approach is applied to the curves measured at the other fields, values are found that are all between $-8 \cdot 10^{-17}$ J/A$^2$ and $-2 \cdot 10^{-16}$ J/A$^2$, within a factor of two from the value from the 10 mT curve and the value obtained in the previous paragraph from the transition from antiparallel to parallel alignment. Actually the approach based on the transition between antiparallel and parallel alignment can be considered as a special case of the coupling field approach. At the transition from parallel to antiparallel alignment the coupling field exactly opposes the applied field, fulfilling equation 4.10. Moreover, the fact that $J_0$ is more or less constant suggests that it is indeed independent of the magnetic moments of EuS and Gd.

One important aspect of interlayer coupling is its dependence on the thicknesses of the layers involved. For such a study a series of samples with exactly the same growth parameters is required. This can be achieved by growing in parallel a set of samples with variable thicknesses of the ferromagnetic layers. In order to obtain a continuous distribution of layer thicknesses, it is best to grow wedge-shaped layers, in which all the layers are still uniform, except for the one for which the thickness is varied (the wedge). Such a sample cannot be measured using a SQUID, but it is very suitable for a MOKE measurement.

Before investigating the dependence of the coupling on the layer thicknesses it is useful to describe a MOKE loop of a EuS/Gd system, as it is not straight-
Figure 4.28: (a) Hysteresis curve of a Ta/Al/EuS(64Å)/Gd(90Å)/Al sample measured by Kerr rotation at a temperature of 5 K. Closed squares indicate the Kerr rotation for increasing fields whereas open circles correspond to decreasing fields. The boxes with the arrows give the orientation of the EuS (lower) and Gd (upper) magnetizations. For this light wavelength (632.8 nm) the sign of the Kerr rotation is opposite for EuS and Gd. (b) So-called inner loop (in black) belonging to the hysteresis curve in panel (a) (added in grey). After the first ferromagnetic layer (EuS) has switched the field is swept back to its starting point.

forward. Figure 4.28a shows a graph of the longitudinal Kerr rotation of a Ta/Al/EuS(64Å)/Gd(90Å)/Al sample. The most striking feature of the MOKE loop is the opposite sign of Kerr rotation upon reflection at these two ferromagnetic materials, as described in equation 3.2. The hysteresis curve in figure 4.28a thus consists of the sum of two loops with opposite sign. Starting at large negative fields (closed squares) first the EuS switches its magnetic orientation, which is visible in the abrupt upward jump in the Kerr rotation. Sweeping the field further leads to a downward slope, associated with the switch of the Gd layer around 80 mT.

Here, yet another method is used to study the interlayer coupling, by measuring inner loops, see figure 4.28b. This provides an additional way to determine the coupling constant $J_0$. In the case of an inner loop, after the switching of the first ferromagnetic layer, which is the EuS, the field is swept back to the starting point. The initially switched ferromagnetic layer will then switch back into its original direction. The inner loop presented in figure 4.28b, indicated in black, corresponds to the full loop from figure 4.28a, that is, for comparison, indicated in grey.

The strength of the interlayer coupling can now be obtained by comparing the inner loop and the full hysteresis curve. For the field sweep in the positive direction (closed squares) the magnetic switching fields are obviously the same, as
the initial state of the system is the same. During the sweep back (open circles) the main difference is the magnetic orientation of the Gd layer. For the inner loop the Gd magnetization points still along the negative field direction, while for the full loop Gd has switched its magnetization and points in the positive field direction. If the coupling is of ferromagnetic nature the EuS magnetization will switch earlier (at “more positive” fields) for the inner loop than for the full loop, and if the coupling is antiferromagnetic it will switch later. At the switching field the magnetostatic energy (per unit area) resulting from the applied magnetic field exactly opposes the internal energy of the system, consisting of coupling energy and other contributions, mainly anisotropy. If again a Stoner-Wohlfarth model is adopted, with uniformly magnetized layers and truly parallel and antiparallel orientations, the switching field for the full and inner loops, \( H_{s,\text{full}}, H_{s,\text{inner}} \), respectively, is given by

\[
-\mu_0 H_{s,\text{full}} M_{\text{EuS}} t_{\text{EuS}} = E_{\text{other}} + J
\]  

(4.12)

\[
-\mu_0 H_{s,\text{inner}} M_{\text{EuS}} t_{\text{EuS}} = E_{\text{other}} - J.
\]  

(4.13)

The only difference between the two situations is the interlayer coupling term. The difference in switching field is thus directly related to the interlayer coupling energy:

\[
H_{s,\text{inner}} - H_{s,\text{full}} = \frac{2J}{\mu_0 M_{\text{EuS}} t_{\text{EuS}}}
\]  

(4.14)

or, alternatively, with \( J = M_{\text{EuS}} M_{\text{Gd}} J_0 \):

\[
J_0 = \frac{\mu_0 (H_{s,\text{inner}} - H_{s,\text{full}}) t_{\text{EuS}}}{2M_{\text{Gd}}}
\]  

(4.15)

Determination of coupling strengths by measuring inner loops is quite common practice in the investigation of interlayer coupling, see for instance Van der Heijden [108] and Yelon [109].

By measuring both full hysteresis curves and inner loops for a Ta/Al/EuS/Gd/Al sample containing a flat 90 Å thick Gd layer and a EuS wedge ranging from 0-160 Å, the coupling energy as a function of the EuS layer thickness can be determined. The result of such an investigation is given in figure 4.29. First of all, the coupling is antiferromagnetic over the whole measurement range, as the shift in switching field is always towards the negative field direction. Moreover, the shift shows a reciprocal behavior with the EuS layer thickness, albeit with an offset in the layer thickness. The offset is yet another indication that part of the EuS is contained in a nonmagnetic interface layer. Here a magnetically dead layer of 20 Å is suggested, which is of the same magnitude as the value from the directly measured magnetic moment (figures 4.23 and 4.24). The reciprocal behavior is exactly in agreement with equation 4.14 if the interlayer coupling energy is assumed to be constant and it can be used to obtain a value of the interlayer coupling constant. If the Gd magnetization around the switching field
Chapter 4. MR based on a EuS spin filter and a ferromagnetic electrode

\[ \mu_0 (H_{inner} - H_{full}) = -\frac{270}{t_{EuS} - 19.7} \mu_0 (\text{mT}) \]

Figure 4.29: Difference in the magnetic switching field of EuS between inner loops and full hysteresis curves (field swept back after EuS switches) for a Ta/Al/EuS/Gd/Al sample containing a EuS wedge and a flat 90 Å thick Gd layer. The curve and equation correspond to a fit with the inverse of the EuS thickness allowing an offset in the thickness, where the EuS layer thickness is in Å and the magnetic induction in mT. For the fit the first data point (at \( t = 44 \) Å) as well as those showing the periodically smaller difference in switching field were ignored.

of EuS (below 10 mT) is estimated from its hysteresis curve to be 200 kA/m, then, using equation 4.15, we find \( J_0 = -1.3 \cdot 10^{-16} \) J/Å² (\( J = 18 \mu J/m^2 \)). Taking into account the uncertainty in this value of around 20%, it is in agreement with the coupling constant obtained from magnetization versus temperature curves and one order of magnitude lower than the value obtained by Rücker et al. for MBE-grown epitaxial EuS(100) on Fe(100) [106]. The high uncertainty originates mainly from the magnetization of the ferromagnetic layers, which is not constant with field or temperature. Since always one of these two parameters is varied in a measurement, the magnetization is not accurately defined.

In a similar fashion, the dependence of the interlayer coupling on the thickness of the Gd layer can be investigated. It turns out that the shift in the EuS switching field resulting from coupling does not depend on the Gd thickness within the error margin of the measurement (not shown here). For a constant exchange energy \( J \) this is in agreement with expectations.

At present, to our best knowledge only one model exists that explains the lack of strong coupling between a magnetic semiconductor and a metallic ferromagnet in direct contact, see also chapter 2. Kneer and Zinn [110] investigated interlayer
coupling between EuS and Ni$_{83}$Fe$_{17}$ (permalloy, Py). For thick EuS layers (> 250 Å) they found that the two layers switched their magnetizations independently, and they calculated that the existence of a Bloch wall inside the EuS along their common interface, was energetically feasible. However, in this way they could explain the absence of a ferromagnetic coupling, not the occurrence of antiferromagnetic coupling as is observed here. Moreover, their theory works for thicker EuS layers only, since the Bloch wall is expected to have a thickness of 400 Å. For the EuS/Gd system that is the topic of this section the absence of a strong direct coupling can perhaps better be explained by the magnetically dead layer at the EuS-Gd interface that spatially separates the two ferromagnetic layers. In any case, still another mechanism must be responsible for the observed antiferromagnetic coupling.

4.8 EuS/Gd interfaces: relevance for spin filter devices

In all measurements discussed in the previous section the interface between EuS and Gd appears to play a crucial role, both for the explanation of the missing magnetic moment, as well as for the motivation for the absence of strong ferromagnetic coupling. A first guess is that the roughness of the EuS layer might be of importance for the existence of this interface layer. Therefore a series of AFM images is shown in figure 4.30 for various EuS thicknesses. As can be seen from the grains in the 30 Å picture the EuS tends to grow crystalline. The grains appear to be fully developed for EuS thicknesses of 30 Å, where the black-white contrast is highest, and where they are most striking. For thicker EuS layers the grains appear to merge as they grow, although the AFM images are not perfectly noise free. The value of the RMS roughness changes similarly: it increases rapidly to 7 Å at a layer thickness of 30 Å, after which it remains more or less constant and even seems to decrease again to 4.7 Å at a layer thickness of 145 Å. The difference between black and white is in each image 40 Å. Deep holes are thus visible in the images shown here, explaining why all EuS tunnel barriers with thicknesses below 60 Å are shorted, as was mentioned in the previous section. Moreover, a RMS roughness of 7 Å means that two-third of the EuS layer has a thickness within a range of 14 Å. Since this corresponds approximately to the thickness of the magnetically dead layer of EuS it is possible that the interface layer consists of the outermost layer of EuS grains together with the material that is deposited in the holes between them. A first check of the charge state of EuS with and without a thin 10 Å Gd cover by XPS did not reveal any change, suggesting that chemical reactions between the two layers are absent.

Finally, the implications of the existence of a nonmagnetic layer at the interface between EuS and Gd on the magnetoresistance of spin filter devices based
**Figure 4.30:** AFM images of EuS grown on Si/SiO$_x$/Ta/Al. The images are 500 × 500 nm$^2$. The label for each image indicates first the EuS thickness, and secondly the RMS roughness of the surface. The black - white contrast corresponds to 40 Å.
on EuS and Gd are discussed. The most prominent aspect of such an interface layer for the electrical properties of the device is its conductivity. If the interface layer is conductive, tunneling will take place from or to this interface layer and the efficiency will be determined by the polarization of interface layer rather than that of the Gd. As the interface is considered to have no magnetic moment, its polarization is almost certainly lower than that of Gd, thereby decreasing the magnetoresistance. If the layer behaves as an insulator on the other hand, it can behave as part of the spin filtering tunnel barrier. In this case the resistance of the device will get higher, as will be explained in chapter 5. The efficiency of the spin filter remains in principle unchanged. The polarization of the electrode depends on the electrode - barrier interface and it is hard to predict whether it will increase or decrease. The magnetoresistance is thus not necessarily affected by this type of interface layer. There is one other aspect of the interface layer that might be of importance. Although the layer in itself is nonmagnetic, it is likely to contain Eu and Gd, that both possess strong localized magnetic moments. While the precise effect of those is not exactly known, they can provide an additional spin flip channel, reducing the magnetoresistance.

In conclusion, it is possible to empirically describe the antiferromagnetic coupling between adjacent EuS and Gd layers if a nonmagnetic interface layer is assumed. AFM measurements suggest that the existence of the interface layer might be due to the roughness of the EuS layer. However, for an explanation of the mechanism behind the coupling between EuS and Gd a more detailed study of this interface layer is required. Also the electrical behavior of EuS spin filter tunneling devices depends on the properties of the interface layer at the EuS - Gd interface. In order to really make a statement about the influence of the interface layer on the magnetoresistance of devices based on EuS and Gd, additional information on the interface layer is needed, such as its composition, magnetic properties, and its conductivity.

4.9 Conclusions

This chapter dealt with the potential of EuS as a spin filtering tunnel barrier. In order to create a magnetoresistance a ferromagnetic electrode was used, such that the resistance depends on the relative magnetic orientation of the spin filter and the ferromagnetic electrode. From a materials study on thin EuS layers it was inferred that growing EuS films at 200°C and annealing afterwards at 430°C leads to the best magnetic and transport ($R \times A = 20 \Omega \text{mm}^2$) properties of the barrier layer. A magnetoresistance ratio of 1.5% has been obtained for a Al/PbS/EuS/PbS/Gd sample, suggesting that the tunnel current through EuS is spin polarized, and that it persists across the PbS. For samples without PbS, e.g. Al/EuS/Gd, a higher magnetoresistance can be achieved. However, it was not possible to reliably produce tunnel barriers for EuS/Gd devices, which is
probably due to the barrier roughness.

In an alternative approach, the bottom electrode could be chosen to be ferromagnetic instead of the top electrode. This should improve the interface between the ferromagnetic electrode and the spin filter. The most promising candidate for the ferromagnetic electrode is Co or CoFe, in combination with an Al₂O₃ buffer layer. However, although the individual layers showed satisfactory magnetic properties, the electrodes were indeed of low resistance, and the barrier layers had indeed a high resistance, no magnetoresistance was observed, probably again due to difficulties in growing smooth EuS tunnel barriers.

The absence of a strong interlayer coupling between EuS and Gd can be explained by the formation of an interface layer between EuS and Gd. A study of the interlayer coupling as a function of the EuS and Gd thicknesses is in full agreement with this picture. Different methods to extract the coupling strength yielded a consistent value of the coupling constant of $J_0 = -1.3 \cdot 10^{-16} \text{ J/A}^2$ ($J = 18 \mu \text{J/m}^2$). However, for a determination of the exact coupling mechanism, as well as for an inventory of the effects of the interface layer on the magnetoresistance of Al/EuS/Gd spin filter tunnel junctions, more information on the nature of this interface layer is required. Properties such as the composition of the interface layer, its electrical conductivity, and its magnetic state are of eminent importance for the coupling mechanism and the (magneto-) resistive behavior of devices.

Altogether, it is possible to produce magnetoresistance devices based on sputter-grown EuS. However, the reproducibility of making working devices is extremely low, probably due to the roughness of the EuS layers. For further research it might therefore be desirable to switch either to another growth method or to another spin-filter material. As to the growth technique, evaporation might be an alternative, as it allows for epitaxial growth with a roughness below a few monolayers, see for instance chapter 6. Lately, the spin filter effect was demonstrated with various other materials (BiMnO₃ and NiFe₂O₄) [23, 25, 89]. Although the growth of these materials is not straightforward either, they might prove to be more suitable as spin filters.
Chapter 5

Magnetoresistance based on a double spin filter

Whereas the previous chapter discussed magnetoresistance devices based on a single spin filter tunnel barrier combined with a ferromagnetic electrode, in this chapter MR devices based on pairs of spin-filter structures will be theoretically discussed. A “double spin filter” device consists of two spin-selective tunnel barriers magnetically separated by a nonmagnetic spacer. The total electric resistance of such a trilayer depends - again - on the relative magnetic orientation of the two spin filters. A double barrier device has two advantages as compared to the single barrier one mentioned in chapter 4. First, the expected magnetoresistance effect is larger than for a single barrier device, unless an exotic electrode is used that is almost completely spin polarized as will be shown below. Second, this device is also of more fundamental interest, since it can be used to demonstrate spin injection in semiconductor materials.

In this chapter calculations are presented on the feasibility of double spin filter magnetoresistance devices. The chapter is divided in two parts. The first addresses the choice of the system and what assumptions are reasonable for a quantitative description of such a system. In the second part the magnitude of the magnetoresistance effect and the spin accumulation will be calculated.

Part of this chapter was also published in Applied Physics Letters [4].

5.1 Introduction

As mentioned in the beginning of this thesis the field of semiconductor spintronics is growing rapidly [6, 7, 111]. One of the major challenges in the field is the achievement of a good efficiency of spin injection into semiconductors, of which first demonstrations have been published during recent years [112–119]. From a conceptual point of view, it has become clear that the most likely fundamental obstacle to inject a spin-polarized current from metals into a semiconductor is
their huge resistance mismatch [37], as described in chapter 2.

The most straightforward solution to this impedance mismatch is to use a different source of spin polarization that has a resistivity closer to that of semiconductors. Although successful spin injection has been achieved in this way, at present the choice of such materials is still limited, even at cryogenic temperatures, whereas at room temperature no such material is readily available at all.

The first successful demonstration of high-efficiency spin injection into a semiconducting material was reported by Fiederling et al. [113] based on the use of a n-doped II-VI diluted magnetic semiconductor (DMS) as the source of a spin-polarized current. II-VI DMS are generally not ferromagnetic, but the application of a magnetic field causes their electron bands to spin split ($g$-factors up to 100), causing unequal populations of spin-up and spin-down electrons in the conduction band. By applying a voltage a spin-polarized current is then led from the DMS into a GaAs quantum well. Recombination of these spin-polarized carriers in the well causes the emission of circularly polarized light, which is used to prove the injection of a spin imbalance into the quantum well. Independently, Ohno et al. [115] achieved spin injection in a similar experiment using a III-V DMS, GaMnAs, as the source of spin polarization. The main difference with the previous experiment is that GaMnAs is ferromagnetic at low temperatures (in this case $T_C = 50$ K), and thus has spin-split electron bands even at zero field. Therefore, by working at low temperatures, the use of large magnetic fields can be avoided.

Another possible route to overcome this impedance mismatch obstacle is to insert a tunneling barrier between the ferromagnet and semiconductor [10, 11]. Spin-polarized tunneling was already explained in chapter 2. In short, a tunnel current depends on the density of states of the contacts at both sides of the barrier. Since the ferromagnet has a spin-dependent density of states, the tunnel current will also be spin polarized, allowing for spin injection into the semiconducting electrode.

First results are available on spin injection through a tunnel barrier, and spin injection into GaAs both through a Schottky barrier as well as through an intentionally added tunnel barrier has been demonstrated. Motsnyi et al. [116] achieved spin injection by electron tunneling from CoFe through an AlO$_x$ tunnel barrier into a GaAs quantum well, again measured by examining the light polarization after recombination of the injected electrons in the well. Mattana et al. [117] injected spins from GaMnAs through an AlAs tunnel barrier into a GaAs quantum well. Detection occurred electrically by addition of a second tunnel barrier and ferromagnet. If spin injection is present, the tunnel current through this sequence of two tunnel barriers depends on the relative magnetic alignment of the two ferromagnets. This way of electrical detection is analogous to the approach in this chapter and will be analyzed in full detail.
Chapter 5. Magnetoresistance based on a double spin filter

Besides spin injection through an explicitly added tunnel barrier, also considerable effort has been put into using the naturally existing Schottky barrier at the metal - semiconductor interface for spin injection. Zhu et al. [118] and Hanbicki et al. [119] injected a spin-polarized current from Fe into a GaAs quantum well through the Schottky barrier at the Fe - GaAs interface. Detection occurred via the polarization of the light emitted upon carrier recombination in the well. However, since the spin polarization of the ferromagnet at the interface with the tunnel barrier is responsible for the spin polarization of the tunnel current, for a ferromagnet - nonmagnetic tunnel barrier combination the junction properties and injection efficiency depend strongly on the metal-barrier interfaces [85].

The use of spin filters

This chapter discusses another, more robust, setup for spin injection in semiconductors, by making use of the spin filter effect of a ferromagnetic tunnel barrier, introduced in chapter 2. This effect was first described by Hao et al. using superconducting electrodes [85] and later by LeClair et al. in combination with a ferromagnetic electrode [5]. In a ferromagnetic semiconductor the magnitude of the bandgap depends on the spin orientation for temperatures below the Curie temperature. Its use as spin filter potentially alleviates the problem of strong interface sensitivity for standard tunnel barriers, as spin filtering is to first order a property of the spin-dependent barrier height alone. Moreover, a magnetic tunnel barrier has the added attractiveness of allowing near 100% (pseudo half-metallic) efficiency of injection (see again chapter 2).

Apart from the possibility of spin injection, as discussed above, magnetic tunnel barriers can also be used to create magnetoresistance devices. Since a spin filter mostly transmits electrons of one spin orientation, the combination of two of them can suppress any current, if the spin filters have an antiparallel alignment. Alternatively, if the two spin filters are oriented in parallel, both transmit electrons of the same spin and a current can flow. Since the magnetization determines the orientation of the spin filters and which (spin-up or spin-down) electrons will be transmitted, the resistance of such a double spin filter system depends on the applied magnetic field. The magnitude of this magnetoresistance effect will be calculated in this chapter.

Besides the two spin filter layers, a spacer layer is required to magnetically separate them from each other. Strictly speaking, the spacer layer can be avoided, but in that case the two magnetic layers would be in direct contact and they would most likely experience a direct ferromagnetic exchange coupling. Even in the absence of such a direct coupling, two compatible semiconducting or insulating ferromagnetic layers would have to be prepared that possess different switching fields in order to be able to magnetically switch them independently. Concerning this spacer layer three different cases can be distinguished, in which the effective
barrier height of the spacer is (I) higher than that of the spin filters, (II) lower than that of the spin filters, or (III) zero. The last case (no barrier resulting from the spacer) occurs if the spacer has states available at the Fermi energy, which is the case for metallic spacer layers. The current through such a trilayer should be described by two tunneling steps, one from the first contact into the spacer and one from the spacer to the other contact. Since the model system that will be discussed contains a PbS spacer and PbS is basically a n-type conductor, this type of system is the central topic of this chapter, and will be discussed in the next section.

If the spacer layer produces a higher tunnel barrier than the spin filters, tunneling always takes place in one step through the complete trilayer, and the spacer has to be considered as a part of this (hybrid) tunnel barrier. This is described by Worledge and Geballe [120], although they do not explicitly put the effect of the spacer layer in their calculation. Their result, including the spacer layer “resistance” is shortly resumed below. The intermediate situation, where the tunnel barrier due to the spacer layer is lower than the barrier in the spin filter, is more complicated. In this case the spacer acts as a quantum well, similar to the situation of a spacer that does not produce a tunnel barrier at all. Depending on the applied voltage a one-step or a two-step (sequential) tunneling process is dominating, and for a correct analysis of the conductivity of such a system both processes should be taken into account. Such systems could lead to exotic effects if the applied voltage is comparable to the (potential) barrier height in the well. Since no carriers are initially present in the well, the electrical injection of electrons of one spin orientation immediately leads to a high spin polarization in the well. However, a treatment of such systems is beyond the topic of this chapter, and the discussion is limited here to situations I and III.

Returning to the case of a spacer with a tunnel barrier that is higher than

![Figure 5.1](image-url)  
**Figure 5.1:** Magnetoresistance device based on two spin filtering layers separated by a nonmagnetic spacer layer forming a single hybrid tunnel barrier. The spacer layer is part of the barrier, i.e. does not influence the conductance by providing quantum well states to the carriers.
the spin filter barrier height, this situation is depicted in figure 5.1. The two spin filters $SF_1$, $SF_2$ are shown, together with the nonmagnetic barrier layer used as a spacer $Sp$, as well as the metallic contacts $M_1$, $M_2$. The layer thicknesses are indicated by $t$ for the spin filters and by $d$ for the spacer. The exchange splitting of the conduction band of the spin filter is $\Delta$, leading to an energy level of the bottom of the conduction band of $U_M \pm \frac{1}{2}\Delta$ for spin-up and spin-down electrons. The energy level of the bottom of the conduction band of the spacer is $U_{NM}$. Electrons tunnel through the complete sequence of spin filter, spacer and spin filter in a single tunneling process. For an evaluation of the magnetoresistance of such a tunnel junction, the conductance $G$ is calculated both for the spin filters in parallel and antiparallel orientation. According to equation 2.13 describing the current as a function of voltage, the conductance is proportional to the squared matrix element and, more specifically, to the transmittance of the barrier. The transmittance of a finite tunnel barrier was given in equation 2.12,

$$T = e^{-2\int \sqrt{\frac{2m}{\hbar^2}|U(x) - E_F|} \, dx}.$$  

Equations 2.18 and 2.19 describe the transmittance of a spin-dependent tunnel barrier for electrons of both spin orientations separately. For a parallel alignment of the magnetization of the two spin filters the transmittance of the full tunnel barrier becomes:

$$T_P = \left( e^{-4t\sqrt{\frac{2m(U_M - E_F - 1/2\Delta)}{\hbar^2}}} + e^{-4t\sqrt{\frac{2m(U_M - E_F + 1/2\Delta)}{\hbar^2}}} \right) e^{-2d\sqrt{\frac{2m(U_{NM} - E_F)}{\hbar^2}}},$$

and for the anti-parallel alignment:

$$T_{AP} = 2e^{-2t\sqrt{\frac{2m(U_M - E_F - 1/2\Delta)}{\hbar^2}}} e^{-2t\sqrt{\frac{2m(U_M - E_F + 1/2\Delta)}{\hbar^2}}} e^{-2d\sqrt{\frac{2m(U_{NM} - E_F)}{\hbar^2}}},$$

where $U_{NM} - E_F$ and $U_M \pm \frac{1}{2}\Delta - E_F$ are the tunnel barrier heights for electrons at the Fermi energy $E_F$ through the nonmagnetic and magnetic layers, respectively, in accordance with figure 5.1.

This approach leads to the following expression for the magnetoresistance MR:

$$MR = \frac{R_{AP} - R_P}{R_P} = \frac{G_P - G_{AP}}{G_{AP}} = \frac{T_P - T_{AP}}{T_{AP}}$$

$$= \frac{1}{2} \left( e^{2t\left(\sqrt{\frac{2m(U_M - E_F - 1/2\Delta)}{\hbar^2}} - \sqrt{\frac{2m(U_M - E_F + 1/2\Delta)}{\hbar^2}}\right)} \right)$$

$$- 1 + \left( e^{-2t\left(\sqrt{\frac{2m(U_M - E_F - 1/2\Delta)}{\hbar^2}} - \sqrt{\frac{2m(U_M - E_F + 1/2\Delta)}{\hbar^2}}\right)} \right) - 1.$$

Equation 5.3 shows that the magnetoresistance is not influenced by the extra resistance due to the spacer layer, since there is no dependence on $d$. The extra
resistance may, however, reduce the applicability of such a system, as it directly contributes to the thickness of the barrier in the single-step tunneling process, on which the resistance depends exponentially. A quantitative estimate will be given below based on the EuS/SrS/EuS system to illustrate this. EuS has a band gap of 1.6 eV with an exchange splitting of 0.36 eV. The barrier height in SrS is estimated to be half the band gap of 4.5 eV. We assume an electron effective mass of 0.4 $m_0$, a value for prototype semiconductors. The resulting magnetoresistance according to equation 5.3 is already 111% for EuS layers of 1.5 nm thickness. However, this configuration with a high barrier spacer layer generally leads to very high resistive junction structures. For high-density MRAM to be commercially attractive the product of resistance and area ($R \times A$) should be below or around $10^4 \Omega \mu m^2$ [121]. A rough estimate based on Simmons’ equation [42] predicts an area resistance of $3 \cdot 10^2 \Omega \mu m^2$ for a 1.5 nm thick EuS tunnel barrier, still within this limit. If an extra 1.5 nm thick EuS layer is added to the barrier, the resistance would increase by a factor of $10^4$. Moreover, the addition of a 1 nm SrS spacer layer would again increase the total resistance of the tunnel barrier by a factor of $10^4$, leading to impractically high values.

**EuS/PbS/EuS spin filter devices**

The device that is the main subject of this chapter and will be considered in detail in the next section consists of a nonmagnetic low-resistive $n$-type semiconductor (PbS) spacer layer that is sandwiched between two larger-gap ferromagnetic semiconductors (EuS) that form the barrier layers. The two barriers are contacted by two metallization layers which form the source and the drain of the device (see figure 5.2). As mentioned before, in this scenario direct ferromagnetic coupling between the two magnetic layers can be avoided by the low-resistive spacer. Moreover, for certain spacer thicknesses an antiferromagnetic coupling between the magnetic layers may be obtained, thus ensuring an adequate control of the relative magnetization. This coupling will be discussed in detail in chapter 6. The antiferromagnetic coupling relieves the inherent technological difficulties related to finding and growing two different but compatible ferromagnetic semiconductor layers with different magnetic switching fields. However, due to the exponential dependence of the interlayer coupling on spacer layer thickness, engineering of the EuS switching fields by interlayer coupling is not trivial.

An additional purpose of this device is to gain insight into the spin transport properties of the nonmagnetic layer (e.g. spin lifetimes), for instance by evaluating the magnetoresistance as a function of the spacer layer thickness. More importantly, it is expected not only to produce a magnetoresistance effect, but it can also be used to electrically show the electrical injection of spins into the PbS quantum well, as will be shown later on. For nonzero applied voltages, spin accumulation is expected to take place in the quantum well for an antiparallel ori-
entation of the spin filters, see also figure 5.2. At the end of the chapter possible applications of this type of quantum well system will be discussed.

As for the physical realization, we propose the EuS/PbS/EuS system as described in chapter 1. To summarize, EuS is a ferromagnetic semiconductor with a Curie temperature of 16.8 K, a semiconducting band gap of 1.6 eV and a spin splitting of the gap of 0.36 eV [83, 85]. PbS is a diamagnetic semiconductor with a narrow gap of 0.4 eV [29]. Despite the disadvantage of a low Curie temperature
that only allows such a device to work at low temperatures, EuS/PbS/EuS is an excellent starting system from both technological and fundamental point of view. First of all, EuS and PbS both crystallize in the rock-salt structure with a lattice mismatch of less than 0.5% and epitaxial growth of EuS/PbS superlattices has already been demonstrated [90]. Secondly, compared to standard DMS materials that require a magnetic induction in the order of Teslas to reach saturation, EuS has a very attractive coercive field that is as low as 2.0 kA/m [98]. With respect to controlling the relative magnetization alignment, it is known that for a certain range of thicknesses of the nonmagnetic PbS layer an antiferromagnetic coupling of the two magnetic layers is induced [58]. This coupling will be the topic of chapter 6.

Another notable advantage of EuS is the very high spin filter efficiency. As the tunneling probability depends exponentially on the barrier height, the tunnel current is expected to be strongly polarized. In order to quantify the efficiency, we define the polarization \( P \) of the EuS tunnel barrier conductance, in accordance with equation 4.6, as:

\[
P = \frac{G_{\text{EuS},\uparrow} - G_{\text{EuS},\downarrow}}{G_{\text{EuS},\uparrow} + G_{\text{EuS},\downarrow}} = \frac{R_{\text{EuS},\downarrow} - R_{\text{EuS},\uparrow}}{R_{\text{EuS},\uparrow} + R_{\text{EuS},\downarrow}}.
\]

(5.4)

\( G_{\text{EuS},\uparrow} \) and \( G_{\text{EuS},\downarrow} \) denote the conductances through the barrier for the spin-up and spin-down electrons, whereas \( R_{\text{EuS},\uparrow} \) and \( R_{\text{EuS},\downarrow} \) are the resistances of the EuS layer for spin-up and spin-down electrons, respectively. It is easy to check, using equations 2.18 and 2.19 and taking into account the proportionality between the conductance and the coefficient of electron transmission through the barrier, that for instance for a 2.5 nm thick EuS barrier, the polarization of the conductance is already 82%. Moreover, the spin injection originates from the difference in barrier heights for spin-up and spin-down electrons and it is not solely due to the spin-dependent interface density of states, as is the case for tunnel contacts based on a magnetic electrode combined with a nonmagnetic barrier. Therefore it should be much more robust to variations in interfacial properties. Even if a dead magnetic layer is present at the interfaces and the effective magnetic barrier thickness is reduced to only a few monolayers, the expected polarization remains present. If a magnetically dead layer is taken into consideration while evaluating the barrier transmission using equation 2.12, the dead magnetic layer only reduces the total transmission (and consequently the conductance) of the tunnel barrier and the current polarization decreases only as a result of the smaller thickness of the ferromagnetic part of the barrier. Thus, as long as the tunneling occurs in a single step, the injection efficiency is only slightly affected. Only if the tunnel transport occurs via impurity states in the dead layer instead of single-step tunneling, the magnetoresistance may decrease significantly, resulting from spin-flip scattering. Scattering at the interface could in principle affect the spin injection efficiency, but on the other hand, there is no reason why this would be more severe in this approach than for structures with a magnetic electrode.
and nonmagnetic barrier. From various single barrier experiments a spin filter efficiency of 80 – 90% was derived using equation 4.6, comparable to the value calculated above [5, 85]. In an ideal, lattice-matched system like EuS/PbS with somewhat thicker spin filters the spin filter efficiency should increase even more, getting close to 100%.

5.2 Magnetoresistance based on a double spin filter system

Many important aspects of the physics of a double spin filter device can be captured in a relatively simple two-current resistance model, in which the current through the trilayer is described as two parallel currents, one of spin-up and one of spin-down electrons. The model is based on two assumptions. The resistance of the spacer layer should be much lower than that of the spin filter layers \( R_{Sp} \ll R_{SF} \), so that there is no voltage drop in the spacer layer. This is not even a necessary requirement, but it is valid for the system under consideration as long as the PbS spacer thickness is not orders of magnitude larger than the thickness of the EuS spin filter, and it allows for a simpler and more intuitive representation of the electrical behavior. The total resistance of the trilayer is then considered to result from two sequential steps in the carrier transport: (tunnelling) from one of the contacts into the quantum well followed by tunnelling from the well to the other contact.\(^1\) Secondly, the electron spin should be conserved upon traveling through the spin filter. Spin flip scattering in the well can be visualized as an extra conductance channel at the position of the well that is the only connection between the two spin-separated branches. As a consequence of both assumptions together, the (chemical) potential for electrons of each spin orientation can be taken constant throughout the well.

The equivalent resistor scheme is depicted in figure 5.3. The electrical current (from left to right) is split in two channels, one for a current of spin-up and one for a current of spin-down carriers. Compared to figure 5.2 both the injector and the detector are represented by two resistances, one for each current channel. Care has to be taken when representing a tunnel barrier by an “ordinary” resistance, as the resistance of a tunnel barrier is not constant with voltage. One should always keep in mind the existence of this voltage dependence of the spin filter resistance, when substituting numerical values. The two current channels are only interconnected in the spacer via the aforementioned spin-flip resistance that will be worked out in the following.

The “spin flip resistance” is derived from a corresponding spin-flip current.

\(^{1}\text{In an alternative approach Saffarzadez [122] recently calculated the magnetoresistance of a double spin filter structure by directly solving the Schrödinger equation for electrons of each spin orientation. She did, however, not take into account any spin flip processes.}\)
Figure 5.3: Resistor model of the proposed double spin filter device. The spin filters are represented by two parallel conductance channels: one for each spin orientation. $R_{1\uparrow}$ and $R_{2\uparrow}$ denote the resistance of both spin filters for the spin-up / spin-down resistance channel.

In the (nonmagnetic) spacer layer unequal populations of spin-up and spin-down electrons can exist, caused by the unequal transmission of electrons of both spin species through the spin filters upon the application of a finite voltage. As a result of this also the spin flip rates for spin-up and spin-down electrons will be different from each other, leading to a net spin flip current. Under the assumption of a constant spin-flip probability the spin-flip current can be written as:

$$ I_{\downarrow\uparrow} = e \frac{n_{\uparrow} - n_{\downarrow}}{\tau_{\downarrow\uparrow}} = e \frac{N(E_F)\mathcal{V}\mu_{\uparrow} - N(E_F)\mathcal{V}\mu_{\downarrow}}{\tau_{\downarrow\uparrow}} = \frac{eN(E_F)\mathcal{V}}{\tau_{\downarrow\uparrow}} (\mu_{\uparrow} - \mu_{\downarrow}), \quad (5.5) $$

where $I_{\downarrow\uparrow}/e$ gives the number of electrons per unit time that flip their spin from up to down, $n_{\uparrow}$ and $n_{\downarrow}$ are the density of spin-up and spin-down electrons, respectively, $\tau_{\text{sf}}$ is the spin-flip time in the quantum well of volume $\mathcal{V}$. $N(E_F)$ is the density of states at the Fermi level, for PbS in the bottom of the conduction band, and $\mu_{\uparrow}, \mu_{\downarrow}$ are the chemical potentials for the two spin directions in the spacer layer, the same as in figure 5.3. The ratio between $I_{\downarrow\uparrow}$ and the voltage difference $(\mu_{\uparrow} - \mu_{\downarrow})/e$ is by definition a conductance and can be written as

$$ R_{\downarrow\uparrow}^{-1} = \frac{eI_{\downarrow\uparrow}}{\mu_{\uparrow} - \mu_{\downarrow}} = \frac{e^2N(E_F)\mathcal{V}}{\tau_{\downarrow\uparrow}}. \quad (5.6) $$

The spin-flip resistance $R_{\downarrow\uparrow}$ relates the potential difference in the well for the two spin species to the spin-flip current, and can as such be implemented in the resistor model, as denoted in figure 5.3. For a numerical evaluation of the efficiency of a device it will turn out to be convenient to rewrite equation 5.6 into...
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the form:

\[ R_{1\uparrow}^{-1} = \frac{e^2 N(E_F)V D}{\lambda_{sf}^2} = \frac{\sigma V}{\lambda_{sf}^2} = \frac{V}{\rho \lambda_{sf}^2} = \frac{1}{R_{Sp}} \cdot t_{Sp}^2, \]

(5.7)

where \( \lambda_{sf} \) is the spin flip length, and \( t_{Sp} \) the thickness of the PbS. The first step is a direct consequence of the diffusive carrier transport in the spacer, since the diffusion length and time scale are related through \( \tau_{\uparrow\downarrow} = \frac{\lambda_{sf}^2}{D} \). The second step involves application of the Einstein relation 2.8 for systems with a partially filled conduction band. Furthermore, the conductivity \( \sigma \) can be replaced with the inverse of the resistivity \( \rho \) and the volume of the spacer is equal to its area multiplied by its thickness. This form will be used later on in this chapter.

A calculation of the electrical behavior of the device can now be based completely on Ohm’s law and Kirchhoff’s relations. Current conservation gives:

\[ I = I_{1\uparrow} + I_{1\downarrow}, \]  
\[ I_{2\uparrow} = I_{1\uparrow} - I_{1\downarrow}, \]  
\[ I_{2\downarrow} = I_{1\downarrow} + I_{1\uparrow}, \]  

(5.8)

(5.9)

(5.10)

where \( I \) is the total current through the device and \( I_{1\uparrow}, I_{1\downarrow}, I_{2\uparrow}, I_{2\downarrow} \), and \( I_{1\downarrow} \) are the currents through the corresponding resistances in figure 5.3. Ohms law applied to these resistances provides five more equations:

\[ V - \frac{\mu_{\uparrow}}{e} = I_{1\uparrow} R_{1\uparrow} \]  
\[ V - \frac{\mu_{\downarrow}}{e} = I_{1\downarrow} R_{1\downarrow} \]  
\[ \frac{\mu_{\uparrow}}{e} = I_{2\uparrow} R_{2\uparrow} \]  
\[ \frac{\mu_{\downarrow}}{e} = I_{2\downarrow} R_{2\downarrow} \]  
\[ \frac{\mu_{\uparrow} - \mu_{\downarrow}}{e} = I_{1\downarrow} R_{1\downarrow} \]

(5.11)

(5.12)

(5.13)

(5.14)

(5.15)

Here \( V \) is the voltage that is applied across the trilayer, and the resistances correspond to those in figure 5.3. This set of eight equations can be solved for the voltage as a function of the total current through the device:

\[ \frac{V}{I} = \frac{R_{1\uparrow} R_{1\downarrow}(R_{2\uparrow} + R_{2\downarrow}) + (R_{1\uparrow} + R_{1\downarrow})R_{2\downarrow} R_{2\uparrow} + R_{1\downarrow}(R_{1\uparrow} + R_{2\downarrow})(R_{1\downarrow} + R_{2\downarrow})}{(R_{1\uparrow} + R_{1\downarrow})(R_{2\uparrow} + R_{2\downarrow}) + R_{1\downarrow}(R_{1\uparrow} + R_{1\downarrow} + R_{2\downarrow} + R_{2\uparrow})} \]

(5.16)

The magnetoresistance of a double spin filter device can be calculated by evaluating this expression both for the case of parallel and of antiparallel alignment of the spin filters. For a parallel magnetic alignment two similar spin filters have equal spin-dependent resistances, i.e. \( R_{1\uparrow} \) equals \( R_{2\uparrow} \) and \( R_{1\downarrow} \) is equal to \( R_{2\downarrow} \).
For an antiparallel alignment the spin-dependent resistances of the two spin filters are equal to those for electrons of the opposite spin orientation of the other spin filter.

In this case both spin filters consist of EuS. In order to simplify notations the polarization \( P \) of the EuS tunnel barrier conductance as it was defined in equation 5.4, is again introduced. Furthermore the spin-dependent resistances \( R_{\text{EuS},\uparrow} \) and \( R_{\text{EuS},\downarrow} \) are naturally related to the real resistance of a single EuS layer \( R_{\text{EuS}} \):

\[
R_{\text{EuS}} = \frac{R_{\text{EuS},\uparrow} R_{\text{EuS},\downarrow}}{R_{\text{EuS},\uparrow} + R_{\text{EuS},\downarrow}}. \quad (5.17)
\]

For the parallel alignment the device resistance is given by

\[
\frac{V}{I} = \frac{2R_{\text{EuS},\uparrow} R_{\text{EuS},\downarrow}}{R_{\text{EuS},\uparrow} + R_{\text{EuS},\downarrow}} = 2R_{\text{EuS}}, \quad (5.18)
\]

and for the antiparallel alignment the resistance equals

\[
\frac{V}{I} = \frac{2R_{\text{EuS},\uparrow} R_{\text{EuS},\downarrow} + (R_{\text{EuS},\uparrow} + R_{\text{EuS},\downarrow}) R_{\|}}{R_{\text{EuS},\uparrow} + R_{\text{EuS},\downarrow} + 2R_{\|}} = \frac{2R_{\text{EuS}}}{1 - P^2 + \frac{2R_{\text{EuS}}}{R_{\|}}}. \quad (5.19)
\]

From equations 5.18 and 5.19 the magnetoresistance ratio follows immediately as:

\[
\text{MR} = \frac{R_{\text{AP}} - R_{\text{P}}}{R_{\text{P}}} = \frac{P^2}{1 - P^2 + \frac{2R_{\text{EuS}}}{R_{\|}}}, \quad (5.20)
\]

using the notations introduced in equations 5.4 and 5.17.

Equation 5.20 is similar to the well-known Julli`ere formula (\( \text{MR} = \frac{2P^2}{1-P^2} \), equation 2.17) for a tunnel junction with a nonmagnetic barrier and two ferromagnetic electrodes. Thus also the role of the spin polarization \( P \) is the same: the higher the polarization, the higher the magnetoresistance ratio. However, as mentioned before, while the spin polarization in ordinary magnetic tunnel junctions is a property of the ferromagnet-barrier interface, the spin-filter polarization can be enhanced by making the spin filter thicker, at the cost of a higher device resistance. Apart from the last term in the denominator, that is associated with spin-flip scattering in the spacer layer, the main difference is the factor of two in the numerator. This is apparently due to the fact that in this case the tunneling is a two-step process, whereas tunneling in a “standard” magnetic tunnel junction is considered to be single-step. An efficient device (large MR) is obtained when the denominator in equation 5.20 is small. Apart from the spin polarization also the spin-flip resistance should be large (\( R_{\text{EuS}}/R_{\|} << 1 \)), visualized in the last term of the denominator.

So far the contribution of the electrical resistance of the PbS spacer to the total resistance of the trilayer was completely neglected. If the resistance of the PbS spacer becomes comparable to the EuS tunnel barrier resistance, the contribution
of the former has to be taken into account and the MR will be reduced. Since spin-flip scattering and the scattering in the spacer that causes its resistance occur simultaneously throughout the spacer, the spacer has to be represented by a network of resistors, thus reducing the transparency of the model. Apart from that, the situation in which the spacer resistance becomes important is only a limiting case of the electrical behavior of the multilayers discussed in this section. Since the spin filters are accounted for as tunnel barriers and the spacer layer as a conductor, the resistance of the former is generally much higher than that of the latter. In practice, for our EuS/PbS/EuS system, the spin-filter resistance is much higher than the resistance of the spacer layer. Therefore, the effect of the contribution of the spacer layer resistance to the total resistance will only be calculated for the case without spin flip in the spacer. The situation depicted in figure 5.4 is considered, that is equal to that in figure 5.3, but without spin flip in the barrier, and with spacer layer resistances $R_{\text{PbS} \uparrow}$ and $R_{\text{PbS} \downarrow}$, both equal to $\frac{1}{2} R_{\text{PbS}}$, in both spin channels. For this configuration the ratio between the magnetoresistance with and without spacer layer resistance can be calculated in the same way as before. This yields

$$\frac{\text{MR}_{\text{eff}}}{\text{MR}} = \frac{1}{1 + \frac{R_{\text{PbS}}}{R_{\text{EuS}}} + \frac{R_{\text{PbS}}^2}{R_{\text{EuS}}(R_{\text{EuS} \uparrow} + R_{\text{EuS} \downarrow})}} \approx \frac{1}{1 + \frac{R_{\text{PbS}}}{R_{\text{EuS}}} + \frac{R_{\text{PbS}}^2}{4R_{\text{EuS}}}}. \quad (5.21)$$

Expression 5.21 can be used to correct the MR in cases where the spacer resistance layer cannot be neglected. Starting from small spacer layer resistances compared to the barrier resistances, a first order correction of the MR ratio in terms of $\frac{R_{\text{PbS}}}{R_{\text{EuS}}}$ will be given by $\text{MR}_{\text{eff}} = \text{MR} \cdot \left( \frac{R_{\text{EuS}}}{R_{\text{PbS}} + R_{\text{PbS}}} \right)$, thus recovering the conductance mismatch predicted by Schmidt et al. [114], see also equation 2.11. Combination of the two above conditions, originating from impedance mismatch and spin-flip scattering in the well ($R_{\text{EuS}} < R_{\downarrow\downarrow}$ together with equation 5.7) gives the range of
spin filter layer resistances for which a high magnetoresistance effect is expected:

\[ R_{\text{PbS}} < R_{\text{EuS}} < R_{\text{PbS}} \cdot \frac{\lambda_{sf}^2}{t_{\text{PbS}}^2}. \]  

(5.22)

The spin injection efficiency conditions derived here are very general, and expected to apply to any spin injection/detection-type device. They are in agreement with the predictions of Fert and Jaffres [11] for the magnetoresistance in metal-insulator-semiconductor-insulator-metal double tunnel junctions. Fert and Jaffres extensively studied the diffusion of electrons and calculated the chemical potential throughout the structure, thus taking into consideration the spatial dependence of the nonequilibrium spin density. They found a maximum in magnetoresistance for barrier resistances of approximately two times the resistance of the spacer layer. Later on, their results will be used for comparison.

In figure 5.5 the effective MR ratio as given in equation 5.21 (last part) is plotted as a function of the ratio \( R_{\text{EuS}}/R_{\text{PbS}} \) for a range of spin-filter polarizations and spacer thicknesses. Realistic values for devices would for instance be \( \lambda_{sf} = 100 \text{ nm} \) (a conservative estimate, taking into consideration values reported in literature for other materials), \( t_{\text{PbS}} = 10 \text{ nm} \), and a spin filter efficiency of 90% as reported by LeClair et al. [5]. The ratio \( R_{\text{EuS}}/R_{\text{PbS}} \) is dependent on the applied voltage due the different transport mechanisms through EuS and PbS (tunneling and drift/diffusion, respectively). For a first calculation of the expected magnetoresistance we take the ratio of spin-filter and spacer-layer resistance to be \( R_{\text{EuS}}/R_{\text{PbS}} = 10 \). With these parameters the expected magnetoresistance should exceed 200%. What is even more relevant is that for a large range of the EuS tunnel barrier resistance, of over two orders of magnitude, the expected effective MR ratio exceeds 100%, confirming the expected stability of the device against any possible variations in the resistance of the spin filter.

Three clear trends in the MR can be observed. First, as expected the MR increases with the spin-filter polarization. Second, the MR decreases upon increasing the PbS spacer layer thickness, due to an increased spin-flip scattering in wider spacers. Third, when looking at the behavior of the MR as a function of the resistance ratio between the barrier and the spacer, it shows a broad maximum at barrier resistances of 3-6 times the resistance of the spacer layer, and then decreases upon increasing the EuS barrier resistance relative to the resistance of the PbS spacer layer, in accordance with the results obtained by Fert and Jaffres [11]. This indicates that, as the probability for electrons to escape via the tunnel barriers decreases, spin flip inside the PbS well becomes of bigger relative importance, which increases the probability that spin information is lost before the electron reaches the drain.

When the magnetizations of the two barriers are aligned in a parallel fashion, the injection and extraction rates are identical and no spin accumulation takes place in the PbS quantum well. If, on the other hand, the alignment
is antiparallel, the injection and extraction rates are different, and therefore a non-equilibrium spin population accumulates, leading to a spin splitting of the chemical potentials, see also figure 5.2. Its magnitude also follows directly from the resistor network calculation, equations 5.8-5.15, that was used to evaluate the magnetoresistance ratio:

\[
\frac{\langle \mu_\uparrow - \mu_\downarrow \rangle}{e} = V \frac{P}{1 + 2R_{\text{EuS}}/R_{\text{PbS}}}.
\]  

(5.23)

For a spin-filter efficiency of about 90\%, a EuS : PbS resistance ratio of 10 and a PbS thickness of around 20\% of the spin flip length the expected spin splitting is in the order of a few tens of mV, assuming an applied voltage of 100 mV. The difference in chemical potential is thus higher than the thermal energy (at 5 K) of 0.4 meV.
The strong spin accumulation may open the door for other applications of this type of device. If an optically active spacer layer with a conveniently chosen band gap is used, the light emitted due to recombination processes in the quantum well will be circularly polarized, which was already used in early spin injection experiments to detect spin injection in a semiconducting quantum well [112, 113, 115, 116, 118, 119]. The sign and degree of circular polarization depends on the spin splitting, therefore it can be controlled by varying the applied voltage according to equation 5.23. A more exotic application can be found in the field of quantum computing. DiVicenzo already proposed a device that reads out single spin quantum bits using a spin filter, potentially EuS, to translate the spin into a charge signal, leading to many novel applications in this field [123].
Chapter 6

Interlayer coupling in EuS/PbS/EuS trilayers

A magnetoresistance device based on a combination of two spin filters has to meet, as mentioned before, several prerequisites. Besides growth-related and practical issues such as the Curie temperature of the spin filters, a more fundamental requirement is the magnetic separability of two spin filters, i.e., they should have different magnetic switching fields, even if they consist of the same material. While for metallic systems the switching fields can be separated using an exchange biasing layer [19, 20], or alternatively, by antiferromagnetic interlayer coupling, for all-semiconductor systems implementation of these two techniques in device-like structures is just starting to be developed. Moreover, for metallic layers interlayer coupling is relatively well understood and described, whereas for systems consisting only of semiconducting layers much less is known.

This chapter deals with antiferromagnetic interlayer exchange coupling in a generic double spin filter EuS/PbS/EuS model system. First, the effect of interlayer coupling in this system will be described. Then a Stoner-Wohlfarth approach to simulate the hysteresis curves will be introduced. Next, the dependence of the coupling on nonmagnetic spacer thickness, on temperature, and, indirectly, on the magnetization of the magnetic layers will be discussed, followed by a qualitative description of the mechanism behind the coupling process.

The contents of this chapter were published as articles in Physical Review B [124] and Journal of Applied Physics [125].

6.1 Introduction

While the interlayer exchange coupling between metallic ferromagnets like Co or Fe across a nonmagnetic metal like Cu or Au is well-studied [49] and is theoretically understood within the Ruderman, Kittel, Kasuya, and Yosida (RKKY) or optical interference model [53, 54], described in chapter 2, interlayer coupling
in multilayers that consist only of semiconducting materials has only recently become an area of intensive research.

Until now interlayer exchange coupling in semiconductor systems has been observed for a limited amount of materials only. Moreover, most of the systems that are known to show magnetic interlayer coupling involve antiferromagnetic materials. First observations of magnetic interlayer coupling were reported in 1994 by Giebultowicz et al. [67] for II-VI type semiconductors. Their neutron scattering experiments showed antiferromagnetic coupling between antiferromagnetic MnTe layers across CdTe spacers. Soon after this, interlayer coupling was also observed in IV-VI EuTe/PbTe multilayers, again by neutron scattering [126]. In this system layers of antiferromagnetic EuTe interact with each other across non-magnetic PbTe layers. This system has become an important model system in the investigation of interlayer exchange coupling. Based on neutron diffraction studies, the effect of lattice strain and interlayer thickness on the coupling were investigated [127]. In the years that followed interlayer coupling was also found and investigated in a number of other nonmetallic systems. By studying (again) neutron diffraction Rhyne et al. discovered coupling in another II-VI structure, MnTe/ZnTe, which is similar to MnTe/CdTe [128]. Van der Heijden et al. studied interlayer coupling for an entirely insulating Fe$_3$O$_4$/MgO structure. Since Fe$_3$O$_4$ has a magnetic spinel structure, it has a net magnetic moment. Because of this, Van der Heijden et al. could study the coupling by directly measuring the magnetic moment of a multilayer [129].

For ferromagnetic semiconductors the amount of systems that show magnetic interlayer coupling is even smaller. As to the III-V semiconductors, ferromagnetic GaMnAs layers in GaMnAs/GaAs/GaMnAs trilayers show only a ferromagnetic interlayer exchange coupling, determined from both neutron scattering and examination of the hysteresis curves [65, 130]. If interlayer coupling is used to modify magnetic switching fields, ferromagnetic coupling between two similar magnetic layers is not suitable, as the switching fields of two equal layers remain the same for ferromagnetic coupling. Instead, antiferromagnetic interlayer exchange coupling promotes an antiferromagnetic alignment and as a consequence causes the switching fields of two similar magnetic layers to differ from each other. The most ideal model system for a study of interlayer coupling is one with antiferromagnetic coupling between two ferromagnetic layers. This was first found in EuS/PbS/EuS and EuS/YbSe/EuS superlattices [58, 130]. At present the EuS/PbS/EuS superlattices and trilayers are the most extensively used model system for studies of interlayer coupling in semiconductors, covering studies of its dependence on layer thicknesses and strain [58, 90, 130]. However, despite these efforts the physical background of the magnetic interlayer coupling is still under debate. For the studies on EuS/PbS/EuS that were mentioned above KCl substrates were used, leading to hysteresis curves with a poorly defined magnetic anisotropy. An improvement is to use lattice-matched PbS substrates. Such an investigation is the subject of this chapter.
6.2 The EuS/PbS/EuS system

The EuS/PbS/EuS trilayer structures described in this chapter were grown epitaxially by electron gun evaporation of EuS and evaporation of PbS from electrically heated tungsten boats at $10^{-7} - 10^{-8}$ mbar. Monocrystalline KCl and PbS substrates with freshly cleaved (100) surfaces were used [131]. During growth the substrate temperature is kept at 250-300°C. The thickness of the layers is monitored \textit{in-situ} with a calibrated quartz resonator\textsuperscript{1}, and is checked after growth by X-ray diffraction analysis.

The detailed design of the trilayer structures studied is as follows: PbS(100) or KCl(100) substrate//PbS(buffer)/EuS($t$)/PbS($d$)/EuS($t$)/PbS(cap) where the thickness of the ferromagnetic layer $t$ is 30-200 Å, and the thickness of the non-magnetic spacer $d$ is 4-90 Å. The 500-1000 Å thick PbS buffer layer accommodates any substrate-multilayer lattice mismatch strain. Finally, the 100-700 Å thick PbS capping layer is intended to protect the trilayer against surface oxidation.

X-ray diffraction analysis (XRD) of the crystalline quality of EuS/PbS/EuS trilayers on PbS [90, 93, 131] shows that these are monocrystalline (100) crystallographically oriented layers with a rocking curve full width at half maximum of about 0.04°-0.08°. For EuS/PbS superlattice-type structures prepared in parallel, the XRD spectra show clear superlattice satellite peaks even up to the 7th order, indicating well-defined planar structures of ultrathin magnetic and nonmagnetic layers. Due to the very good lattice match (closer than 0.5 %) between EuS and PbS these semiconductor materials can be grown pseudomorphically up to a total thickness of about 2000 Å.

Previous studies have shown that the interdiffusion at the EuS-PbS interface is low and corresponds to an intermixing of only 1-2 monolayers [90]. Therefore, the main morphological defects at the interface are expected to originate from various steps inevitably present in the substrate surface. An atomic force microscopy (AFM) analysis of the freshly cleaved (100) surfaces of KCl and PbS substrate crystals shows flat regions attributed to terraces of the cleaved substrates (root mean square, RMS, roughness of 10 Å) for an area of up to 10x10 µm\textsuperscript{2}. These regions are separated by few-monolayer high steps. The cleaved surfaces show also larger (0.1 µm) steps but these are located at macroscopically large distances (of the order of 100 µm). AFM analysis of the complete samples exposed to air shows a RMS surface roughness of about 40 Å (for the area of 10x10 µm\textsuperscript{2}) presumably due to surface oxidation of the PbS cap layer.

The magnetic properties of the EuS/PbS/EuS trilayers were measured by SQUID magnetometry. Hysteresis curves at various temperatures as well as the magnetic moment as a function of temperature for different applied fields were measured. Before turning to the EuS/PbS/EuS trilayers that show interlayer

\textsuperscript{1}The addition of material on a quartz resonator shifts its resonance frequency by an amount that is a measure for the thickness of the deposited layer.
coupling, first an uncoupled system will be discussed.

Hysteresis curves measured along a [110] and a [100] axis of two uncoupled EuS layers (in a EuS(30 Å)/PbS(50 Å)/EuS(30 Å) system) are depicted in figure 6.1a. A first observation could be that in general, at low temperatures, all samples show a saturation magnetic moment within 10% of the expected moment for an ideal EuS layer (7 $\mu_B$/atom), confirming the high quality of the samples. The rock-salt structure of EuS leads to a cubic, in-plane magnetic anisotropy. Indeed, for the loop along the [110] axis the magnetization switches to almost the full saturation value, whereas the magnetic moment measured along the [100] axis switches only to roughly 0.7 times the saturation magnetic moment, corresponding, as expected, to a magnetic moment that is 45° off the field direction.

Figure 6.1 also shows that the coercive field of such EuS layers is typically 2 mT. At fields of the order of 10 mT, however, the magnetic moment has not completely reached saturation. We ascribe this to the existence of domains of low formation energy in EuS, an effect that has been known for a long time already for EuS, and is supposed to be due to the relatively small exchange interaction in the material [110].

Figure 6.1 also shows hysteresis curves for a EuS(30 Å)/PbS(11 Å)/EuS(30 Å) trilayer. In this case a plateau of low magnetic moment is clearly visible for applied magnetic fields below 2 mT. This corresponds to a nearly antiparallel orientation of both EuS layers, a feature of antiferromagnetic interlayer coupling shown by all (a few dozen) samples with PbS spacers between 6 and 12 Å. Figure 6.1 also shows that for the layers grown on PbS substrates a clear difference can be observed between measurements with the field along the in-plane [110] and [100] directions, in agreement with the cubic anisotropy of EuS. For EuS layers grown on KCl there is almost no difference in the hysteresis loops measured along [110] and [100] axes. A recent neutron reflectometry study by Kepa et al [132] on the anisotropy within the sample plane indicates for samples grown on KCl substrates that EuS-PbS superlattices have [210] and [120] easy axes. An unequal population of domains along these axes suggests that the cubic symmetry of the anisotropy is in this case lifted.

Although the width of the plateau of low magnetic moment is generally slightly larger for trilayers on KCl substrates with respect to the same trilayers grown in parallel on PbS substrates, in this chapter we will focus on the trilayers on PbS substrates since the anisotropy is better defined there, and, as a consequence, the switching field between the antiparallel and the parallel alignment of the EuS layers can be determined more accurately. How to extract physical information from the hysteresis curves is the topic of the next section.
Figure 6.1: (a) Hysteresis curves at 5 K measured in-plane along [110] and [100] axes for a EuS(30Å)/PbS(50Å)/EuS(30Å) trilayer grown on a PbS substrate and covered with a PbS capping layer. (b) Similar hysteresis curves as in panel (a) for a EuS(30Å)/PbS(11Å)/EuS(30Å) trilayer. (c) Hysteresis curves for the same trilayer as in panel (b), but in this case grown on a KCl substrate.
6.3 Modeling the hysteresis loops and the temperature dependence of the magnetization

In order to study interlayer coupling quantitatively as a function of various parameters such as spacer layer thickness and temperature, a model was developed for the specific situation of EuS/PbS/EuS trilayers. In this section the modeling procedure will be explained by focusing on one sample that can be considered representative for all trilayers with PbS spacers between 4 Å and 12 Å. This sample contains two 40 Å thick EuS layers separated by a 2.5 monolayer (7.5 Å) thick PbS spacer layer. Figure 6.2 shows both the hysteresis curve and the magnetization versus temperature for different fields.

Due to the antiferromagnetic exchange interaction between the EuS layers, in small fields the magnetic layers align antiparallel with respect to each other’s magnetization, which leads to the plateau in figure 6.2. The field at which the antiparallel configuration of the EuS layer magnetizations is transformed to a parallel orientation will from now on be referred to as the switching field $H_s$. This field plays an important role in a quantitative determination of the exchange energy, as will be demonstrated below. A similar effect can be observed in the temperature dependence of the magnetic moment (see fig. 1b). For small applied

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**Figure 6.2:** (a) Easy axis hysteresis curve at 5K for a EuS(40Å)/PbS(7.5Å)/EuS(40Å) sample. $H_s$ is the average switching field between parallel and antiparallel alignment and $\chi_0$ is the zero-field susceptibility. The arrows denote the alignment of the magnetizations of the two EuS layers. The grey solid line represents a hard-axis curve, which is not further discussed. (b) Magnetization versus temperature measurements along a hard axis in a constant field.
fields, the magnetization shows a sharp decrease in magnitude below a certain temperature. This is related to a change from a ferromagnetic alignment of the magnetizations of the EuS layers (approximately) along the direction of the magnetic field, to an antiferromagnetic alignment of the two magnetic layers (almost perpendicular to the field). This will be discussed at the end of this section.

A Stoner-Wohlfarth-like model is introduced in order to quantitatively analyze the magnetization data. In a Stoner-Wohlfarth model the magnetization of magnetic layers is taken to be uniform throughout the layers. Hysteresis curves are then simulated based on a calculation of the total magnetic energy. For this system, besides the magnetostatic energy and the fourfold (cubic) anisotropy, also the interlayer exchange energy is accounted for [133, 134]. The total magnetic areal energy density $E/A$ of two identical, single-domain EuS layers with a thickness $t$ and a saturation magnetization $M$ is then given by:

$$E/A = -\mu_0 HM t \cos(\vartheta_1 - \vartheta_H) - \mu_0 HM t \cos(\vartheta_2 - \vartheta_H)$$
$$+ K_c t \sin^2 \vartheta_1 \cos^2 \vartheta_1 + K_c t \sin^2 \vartheta_2 \cos^2 \vartheta_2$$
$$- J \cos(\vartheta_1 - \vartheta_2),$$

(6.1)

where the applied magnetic field is denoted by $H$, and $\vartheta_H$, $\vartheta_1$, and $\vartheta_2$ are the angles of the field and the magnetizations of each magnetic layer with respect to a reference axis, respectively, see figure 6.3. The choice of the direction of the reference axis is free, in principle. As a convention, we used the direction of the easy anisotropy axis. $K_c$ denotes the cubic anisotropy energy per volume unit, and $J$ is the interlayer exchange energy per unit of surface area.

A magnetization curve can be obtained by minimizing for each applied field the areal energy density (see equation 6.1) with respect to the magnetization
Figure 6.4: Model calculations simulating the field dependence of the magnetic moment of a EuS(40Å)/PbS(7.5Å)/EuS(40Å) sample at 5 K for a magnetic field along the easy [110] crystal axis: (a) the influence of the exchange energy $J$ for $K_c = 9$ kJ/m$^3$, and (b) the influence of the anisotropy $K_c$ for $J = -7$ µJ/m$^2$. The inset in panel (b) is a zoom of the behavior at small fields.

In order to provide more feeling for the effect of the parameters $K_c$ and $J$ on the simulated magnetization curves, simulations for the EuS(40Å)/PbS(7.5Å)/EuS(40Å) sample for several values of the exchange energy and anisotropy are shown in figure 6.4. Figure 6.4a shows that, upon increasing the exchange energy, the width of the plateau of antiferromagnetic alignment becomes larger. The anisotropy determines how tightly the magnetizations of both layers are confined to the easy axes in the antiferromagnetic alignment (a spin-flop state), and therefore determines the zero-field susceptibility, visible in the slope of the curve for small fields, see figure 6.4b.
The simulations plotted in figure 6.4 will now be compared to the measured hysteresis curves of the same EuS/PbS/EuS trilayer shown in figure 6.2a. A simulation that describes the magnetic behavior best should at least have the same switching field $H_s$, as well as the same zero-field susceptibility $\chi_0$ as the measured curve, as indicated in figure 6.2a. This is why we used these two parameters as the criterion to select the best simulations. Since the plateau width is very sensitive to the exchange energy, the fit accuracy is mainly determined by the uncertainty in determining the switching field from the experimental curve. This is limited by the intrinsic non-ideal behavior of the hysteresis loop of a single EuS layer, cf. figure 6.1a, as the hysteresis curve of a single layer is also approaching its saturation value relatively slowly for high applied fields, like the one of the trilayer. Similarly, the accuracy in the determination of the anisotropy depends on the uncertainty in the measured zero-field susceptibility, which will be overestimated if the two EuS layers do not have exactly the same magnetization. The fit thus provides a lower boundary for the anisotropy energy. The simulation with $J = -7 \, \mu J/m^2$ and $K_c = 9 \, kJ/m^3$ produces the best fit for the typical measurement shown in figure 6.2a.

In order to simulate the temperature dependence of the magnetic moment, also the temperature dependence of the saturation magnetization, anisotropy, and exchange needs to be taken into account. The saturation magnetization of the individual EuS layers generally follows a mean-field behavior [135]. Magnetic crystalline anisotropy has been the topic of several theoretical as well as experimental studies [137]. Although early theoretical considerations led to a 10th order power-law dependence of the anisotropy energy on magnetization (derived for metallic systems), more recent experimental observations suggest a lower (3rd-4th) power dependence [137]. Also for this system the hysteresis curves confirm this strong dependence of the anisotropy on the magnetization. Therefore, the anisotropy is described in our model by a power law [135]. For the interlayer exchange coupling a similar finding will be described in section 6.5, where we discuss the dependence of both the magnetization and the interlayer exchange coupling energy on temperature; in advance of this, it is assumed in the model that the interlayer exchange coupling can also be written as a power of the layer magnetization.

Figure 6.5 shows the results of such simulations for the same sample, for which the measured curves were shown in figure 6.2b, with the magnetic field along a hard [100] axis. Panel 6.5a shows simulations for different applied fields. The simulations reproduce the qualitative behavior of the total magnetic moment. For high fields a monotonous increase with decreasing temperature is found, cor-

\[2\text{Mean-field theory is one of the most elementary approaches to describe the temperature dependence of the magnetization of a magnetic material. In mean-field theory the exchange interactions between the individual magnetic moments in a material are represented by an effective magnetic field, the mean field [136].}\]
Figure 6.5: Model calculations of the net magnetic moment as a function of temperature for a EuS(40 Å)/PbS/EuS(40 Å) system for a magnetic field along the hard [100] crystal axis: (a) the impact of the magnetic field $H$ for $J \sim M^{5.7}$ and (b) the influence of the exponent in the expression $J \sim M^{\exp}$. The anisotropy energy $K_c$ is taken to be $K_{c\text{eff}} = K_c (M/M_s)^4$ as reported previously [135].

responding to a parallel alignment of the magnetic moment of the two layers. For relatively low fields the simulations predict an initial increase, followed by a decrease of the total magnetic moment, due to a change from a parallel to an antiferromagnetic alignment of the two magnetic layers. Variation of the exponent in the power-law dependence of $J$ on the layer magnetization $M$ changes the general shape of the magnetic moment versus temperature curve and the temperature at which the maximum magnetic moment is reached, see figure 6.5b. A special case is $J \sim M^2$. If anisotropy is neglected, the effect of an increasing saturation moment of the layers will, below a certain temperature, exactly be compensated by a rotation of the magnetization directions away from each other and from the field direction, leading to a constant net magnetic moment. If anisotropy is taken into account, a monotonous increase in magnetic moment is expected, from which we conclude that the experimental dependence of $J$ on magnetization/temperature is stronger than quadratic, see figure 6.2b. A discussion of the temperature dependence of the interlayer coupling will be the topic of section 6.5, and then also the mechanism behind the interlayer coupling will be discussed.

It should be emphasized that the present model can qualitatively describe the magnetic moment versus temperature dependence, but it cannot describe the exact quantitative behavior for all applied fields, as shown in figure 6.2, with
Chapter 6. Interlayer coupling in EuS/PbS/EuS trilayers

the same set of parameters. The most probable cause is the use of a Brillouin function describing the temperature dependence of the magnetization. For small applied fields the magnetization of a single EuS layer, see figure 6.1a, is not saturated, with a magnitude depending on the applied field and its orientation. If the two EuS layers are not in parallel, they experience a magnetic field at a different orientation with respect to their own magnetizations, and therefore the two layers may have unequal magnetic moments. If a more accurate description is required, the Brillouin function can be replaced with a more realistic function, accounting for the dependence of the magnetization on the field and its relative orientation.

Generally, simulations for other samples lead to exchange energies in the order of 1-50 $\mu$J/m$^2$ at low temperatures, in fair agreement with available neutron reflectivity data for spacer thicknesses between 7 Å and 12 Å [58]. However, for thinner spacers the values from the simulations are lower than those from neutron reflectometry, an effect that can be ascribed to ferromagnetic interlayer coupling via pinholes in the spacer layer. The dependence of the interlayer exchange coupling on spacer layer thickness will be the topic of the next section.

6.4 Variation of spacer layer thickness

Most of the mechanisms behind interlayer coupling have their own distinct dependence on the thickness of the spacer layer (see also chapter 2). Therefore, we start the investigation of the underlying physics of the interlayer coupling with its dependence on the thickness of the nonmagnetic spacer. Figure 6.6 summarizes the results of such an investigation. The data are obtained by simulating the hysteresis loops of several EuS/PbS/EuS trilayers with various spacer thicknesses, using the method described in the previous section. Considering the sign of the interaction to start with, the interlayer exchange coupling is, if present, always found to be antiferromagnetic. The values of the interlayer exchange coupling energy $|J|$ obtained from the simulations are of the order of $10^{-3}$ – $10^{-2}$ mJ/m$^2$ for PbS spacer thicknesses in the range of 4 to 11 Å. Trilayers with thicker spacers did not show any measurable interlayer coupling.

Of all descriptions of interlayer exchange coupling, the RKKY theory is the most common, describing the thoroughly investigated metallic systems. As mentioned in chapter 2, the RKKY theory predicts an oscillating interlayer exchange coupling as a function of the thickness of the nonmagnetic spacer scaling with the local carrier concentration (a higher carrier concentration leads to a shorter period of the oscillation) [59]. The interaction starts being ferromagnetic for the thinnest spacer layers. Jungwirth et al. calculated that the RKKY interaction leads to a ferromagnetic coupling for all spacers up to 30 Å for a carrier concentration of $10^{20}$ cm$^{-3}$ or lower [59]. Since the carrier concentration in the PbS spacer layers discussed here is $10^{18}$ – $10^{19}$ cm$^{-3}$, the interlayer coupling should
be ferromagnetic for all spacer thicknesses investigated, while an antiferromagnetic coupling is observed for spacers as thin as 4 Å thickness. Therefore RKKY can already be excluded as a potential mechanism describing the coupling in EuS/PbS/EuS.

Blinowski and Kacman predicted an antiferromagnetic interlayer exchange coupling based on a calculation of the spin-dependent total energy of the valence electrons of the EuS/PbS/EuS structure [70]. The observed interlayer exchange coupling is one order of magnitude weaker than predicted within their model (see figure 6.6). However, the model assumed perfectly flat layers with an integer number of atomic monolayers in the spacer layer. Although the coupling mechanism in metallic multilayers is different from the mechanism in these semiconductor trilayers, at least for metallic multilayers it has already been reported that alloying effects at the interfaces decrease the coupling strength considerably [138], and such an effect could also be present in the case of semiconductors. As can be seen from figure 6.6, the interlayer exchange coupling energy appears to reach

Figure 6.6: Overview of the measured antiferromagnetic interlayer exchange coupling energy $|J|$ as a function of the PbS spacer layer thickness in EuS/PbS/EuS trilayers. Closed squares correspond to samples grown on PbS, open diamonds to those on KCl substrates. Grey corresponds to easy axis measurements and black to those along hard axes. The EuS thickness varied between 30 and 60 Å. For comparison, values from neutron diffraction measurements on EuS/PbS superlattices grown on PbS substrates [58] (full circles) as well as the theoretical prediction by Blinowski and Kacman [70] (crosses) are also plotted. The lines are only guides to the eye.
a broad maximum for spacer thicknesses around 2.5 monolayers (7.5 Å). For thicker spacers the measured values are consistent with those found in neutron reflectivity measurements [58]. Moreover, the decrease in the coupling energy with increasing spacer thickness is in qualitative agreement with the calculations of Blinowski and Kacman [70], although any detailed comparison with theory is not possible due to the rather large spread of our data, although this spread is partially due to differences in substrate. In section 6.6 a further discussion of the coupling mechanism will be presented.

For thinner spacer layers (< 7.5 Å) the magnitude of the interlayer exchange coupling energy becomes slightly smaller again, contrary to the neutron reflectivity data. For these low spacer thicknesses, corresponding to 1-2 monolayers of PbS, the existence of pinholes is very likely, potentially causing strong local ferromagnetic interactions between the two magnetic layers. Measurements of the magnetic moment are sensitive to the net moment of the whole sample and therefore do not separate ferromagnetically and antiferromagnetically coupled regions in the trilayer, resulting in an averaged, smaller value of the interlayer exchange coupling energy in this regime of thin (< 7.5 Å) spacers. The neutron reflectivity results in figure 6.6 monitor only local antiferromagnetic alignment between the magnetic layers in the sample, which is insensitive to the presence of local ferromagnetic coupling in other regions of the sample.

Summarizing, the interlayer exchange coupling energy is reduced as the spacer thickness increases in the range above about 7.5 Å, in qualitative agreement with the calculations by Blinowski and Kacman [70]. However, for very thin spacer layer thicknesses the net interlayer coupling energy decreases, most probably due to the existence of pinholes in the PbS, resulting in a mix of a strong local ferromagnetic interaction and an antiferromagnetic coupling elsewhere, leading to a smaller average coupling strength.

### 6.5 Temperature and magnetization dependence

A second route in the investigation of the interlayer exchange coupling in EuS/PbS/EuS trilayers is to study its temperature dependence in a systematic way. If one takes into consideration the microscopic origin of the coupling, the relevant quantity to study is not the interlayer exchange coupling energy \( J \), but rather the exchange coupling constant \( J_{\text{exch}} \), defined as

\[
J = J_{\text{exch}} \sum_{i,j} \vec{S}_i \cdot \vec{S}_j.
\]

The summation is taken over all spins at the interface between the magnetic layers (\( i \in \text{layer 1 and } j \in \text{layer 2} \)). As the exchange coupling between neighboring spins within the same EuS layer is expected to be much stronger than the exchange coupling across the nonmagnetic layer, the local correlations between spins across layers can be neglected. As a direct consequence the summations over spins can be replaced with the average magnetizations and \( J_{\text{exch}} \) should be proportional to \( J/M^2 \).
Figure 6.7: Easy axis [110] hysteresis loops for a EuS(60Å)/PbS(6Å)/EuS(60Å) trilayer for different temperatures below the Curie temperature. In addition simulated curves using a Stoner-Wohlfarth model are drawn showing a fair qualitative agreement with the experiment in the region of antiferromagnetic coupling.
For a systematic study of the temperature dependence of the interlayer coupling hysteresis loops were measured at several different temperatures with the magnetic field applied along the easy [110] crystal axis. As an extra illustration of the modeling, figure 6.7 shows the hysteresis curves for a EuS(60Å)/PbS(6Å)/EuS(60Å) sample. An antiparallel alignment of the two magnetic layers is again visible through the low-field plateau. Clearly the width of this plateau resulting from antiferromagnetic coupling diminishes with increasing temperature.

The simulated curves are shown as additional solid lines in figure 6.7. The agreement between simulation and experimental data is reasonably good for low applied magnetic fields. As explained in section 6.3 the width of the plateau of antiferromagnetic alignment (i.e., the switching field) is mainly determined by the interlayer exchange coupling, while the zero-field susceptibility (i.e., the slope of the plateau) is mostly determined by the anisotropy energy. Therefore, by fitting the low-field behavior, the interlayer exchange coupling energy $J_{\text{exch}}$ and the crystalline anisotropy $K_c$ are determined.

As was already described in section 6.3, saturation of the total magnetic moment as a function of the applied magnetic field is reached slower than what is generally observed in metallic multilayers [49], in accordance with the loops of an uncoupled EuS layer (Fig. 6.1a). The field at which the transition towards a ferromagnetic alignment of the EuS layers is completed is thus hard to define, again motivating our choice to use the low-field behavior for our simulations.

One might expect that the microscopic coupling is temperature and layer magnetization independent ($J_{\text{exch}} = \text{constant}$). In this case $J/M^2$ remains constant as a function of temperature. However, the discussion of the total magnetization as

![Figure 6.8](image)

**Figure 6.8:** Antiferromagnetic interlayer exchange coupling constant as a function of temperature for a EuS(60Å)/PbS(6Å)/EuS(60Å) sample. The inset shows the behavior of the saturation magnetization of a single layer as a function of temperature.
Figure 6.9: Antiferromagnetic interlayer exchange coupling constant (coupling energy $J$ divided by $M^2$) plotted on a double logarithmic scale as a function of the saturation magnetization of the EuS layers for EuS(60Å)/PbS(6Å)/EuS(60Å) (open diamonds), 60Å/9Å/60Å (closed diamonds), and 40Å/7.5Å/40Å (open circles) trilayers. Note that the horizontal shift is due to different sample areas.

a function of temperature in section 6.3 already indicated that the interlayer exchange coupling was actually temperature or magnetization dependent (see also Chernyshova et al [135]). In order to investigate this dependence in more detail the interlayer exchange coupling constant $J_{\text{exch}}$ can be plotted as a function of temperature. Figure 6.8 shows such a plot for the EuS(60Å)/PbS(6Å)/EuS(60Å) sample, extracted from the hysteresis curves as shown in figure 6.7. The interlayer exchange coupling constant indeed displays a strong dependence on temperature, showing a qualitatively similar behavior as the saturation magnetization of the EuS layers, plotted in the inset of figure 6.8.

In order to further quantify this, the log-log plot of the antiferromagnetic interlayer exchange coupling constant $J_{\text{exch}}$ as a function of the saturation magnetization of the EuS layers is shown in figure 6.9 for three individual samples. For all three samples a clear power law dependence can be observed, with an exponent around 1.8-1.9 for the two samples with a 60 Å thick EuS layer, and a smaller exponent (1.4) for the sample with the thinner (40 Å) EuS layer. One might speculate about a dependence of the coupling constant on the EuS layer thicknesses. However, a more detailed study would be required to draw firm conclusions on this issue. It still appears that the power-law behavior on the layer magnetization must be considered as an intrinsic property of the interlayer coupling mechanism in EuS/PbS/EuS trilayers, although a conclusive theoretical model is lacking. For a comparison with another system: the coupling in Fe/EuS
was investigated by U. Rücker et al [106]. Writing their data on the interlayer exchange coupling constant in a similar fashion as was done for EuS/PbS/EuS, it turns out that the interlayer exchange coupling constant can be approximated by a power on the EuS magnetization of 0.5 only. Part of the discrepancy is of course resulting from the fact that they only have one EuS layer in their system. However, the squared dependence, a power of 1.0, is still much less then what is observed here, indicating that for their systems a different coupling mechanism is involved.

For a confirmation of this intrinsic temperature dependence of the interlayer coupling, the net magnetic moment of the trilayer $\mu$ was also directly measured as a function of temperature for different applied magnetic fields, as was described in section 6.3. A plot is given in figure 6.10 for the EuS(60Å)/PbS(6Å)/EuS(60Å) sample under discussion. For large applied magnetic fields, the magnetization shows a monotonic increase as temperature decreases, consistent with a parallel alignment of the two magnetic layers. In contrast, for lower applied fields, the magnetization shows a sharp decrease in magnitude below a certain temperature, as a consequence of a change from ferromagnetic to antiferromagnetic alignment of the two magnetic layers.

It was already discussed in section 6.3 that, if one neglects the anisotropy and assumes the interlayer exchange coupling energy $J$ to depend only on the square of the magnetization, the magnetic moment of the sample remains constant below a certain temperature. This is equivalent to the situation of a constant interlayer exchange coupling constant $J_{\text{exch}}$. For finite values of anisotropy, a monotonous increase of the total magnetic moment during cooling is expected for all applied
fields. In contrast, this sample is showing a sharp decrease in the magnetic moment below a certain temperature indicating an intrinsic dependence of the interlayer exchange coupling constant on either temperature or magnetic moment of the layer, which is a straightforward confirmation of what was extracted from the analysis of the hysteresis curves. If the data set in figure 6.10 is simulated with a curve like those in figure 6.5, the interlayer coupling constant is found to depend on the EuS magnetization by a 4th to a 6th power. However, the determination based on the magnetic hysteresis curves is more accurate than based on the magnetization as a function of temperature.

6.6 The origin of the interlayer coupling

At present the exact physical origin of the antiferromagnetic interlayer exchange coupling in systems like EuS/PbS/EuS is not yet known and theoretical predictions on its temperature dependence are not available. For convenience the interlayer coupling models described in chapter 2 will be shortly reviewed here. In metallic systems, the interlayer coupling is described within the RKKY model [139], and the temperature dependence of the interlayer exchange coupling constant stems from the broadening of the Fermi-Dirac distribution with increasing temperature. In p-type semiconductor systems, the coupling between spins is mediated via the holes in the valence band [59]. However, calculations by Jungwirth et al. indicate that carrier-mediated interactions lead to a ferromagnetic coupling for the carrier concentrations and spacer layer thicknesses of the samples discussed in this chapter [59], while an antiferromagnetic interlayer exchange coupling is observed in EuS/PbS/EuS trilayers. Therefore this type of interlayer exchange coupling mechanism can be excluded here. For II-VI semiconductor structures the interlayer exchange coupling was explained by interaction via shallow donor impurities, which have, however, never been detected for PbS [68, 69]. A potential mechanism for interlayer exchange coupling would be a Bloembergen-Rowland type mechanism, where the exchange interaction is mediated via virtual excitations in the PbS spacer. However, this mechanism leads again to a ferromagnetic interlayer exchange coupling [66], in contrast to the observed antiferromagnetic coupling.

The observed temperature dependence of the interlayer exchange coupling constant can at least qualitatively be understood under the assumption that the coupling is determined by changes in the bandstructure of the full EuS/PbS/EuS heterostructure induced by the exchange splitting of the \( d \)-type bands of EuS. This line of reasoning is also the basis of the calculations by Blinowski and Kacman, who actually take into account the exchange splitting of all bands in EuS [70]. In a simple one-electron picture, as is shown in figure 6.11, the energy of the states inside a quantum well depends on the barrier height, and one therefore expects that the total free energy will depend on the exchange splitting in EuS.
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Figure 6.11: Schematic drawing of the effect of the exchange splitting of the EuS conduction band on the energy of the conduction band in the PbS quantum well. As result of the exchange splitting of EuS, electrons of different spin orientation inside the quantum well will experience different barrier heights and the will therefore possess different energies.

Thus, as the interlayer exchange coupling energy is determined by the difference in the total free energy between the parallel and the antiparallel configuration of the EuS magnetizations, it is expected to depend on the exchange splitting of the \( d \)-like bands in the EuS. Since the exchange splitting in EuS is approximately proportional to the magnetization, the interlayer exchange coupling energy should also depend on magnetization via the exchange splitting of the bands [17]. To first order, the difference in the total free energy between the parallel and the antiparallel configuration can be considered to be proportional to the exchange splitting of both magnetic layers, and the interlayer exchange coupling constant can be written as:

\[
J_{\text{exch}} \propto \Delta_1 \Delta_2 \propto M_1 M_2, \tag{6.2}
\]

where \( \Delta_1 \) and \( \Delta_2 \) denote the exchange splitting of both magnetic layer and \( M_1 \) and \( M_1 \) are the corresponding magnetizations. The above reasoning suggests a \( (M^2) \) higher-order dependence of the interlayer exchange coupling energy on the magnetization of the EuS, more in agreement with the experimental values reported in figure 6.9. A recent theoretical study following this line of reasoning indeed shows a tendency for an antiferromagnetic interlayer exchange coupling, but only for larger PbS spacer thicknesses or much higher carrier densities in the well than is the case in the EuS/PbS/EuS trilayers discussed here [140]. When the splitting of all bands, including the valence band, is taken into account and realistic band structures are used, the correct sign of the exchange coupling energy is indeed obtained, as shown by Blinowski and Kacman in their calculations [70].
6.7 Conclusions

The antiferromagnetic interlayer exchange coupling in high-quality epitaxial EuS/PbS/EuS trilayers was investigated by means of SQUID magnetometry. The value of the interlayer exchange coupling energy was determined by simulating the hysteresis curve based on a Stoner-Wohlfarth model. Apart from growth-related issues special attention was given to its dependence on spacer thickness and temperature. In trilayers with a PbS thickness between 4 and 12 Å the low temperature hysteresis loops show the signature of antiferromagnetic coupling. For spacer thicknesses exceeding 2.5 monolayers (7.5 Å) the interlayer exchange coupling energy diminishes with increasing spacer layer thickness, in agreement with data obtained from neutron reflectometry measurements [58] and the calculations by Blinowski and Kacman [70]. For thinner spacer layers the antiferromagnetic interlayer exchange coupling energy decreases again, an effect that is most likely due to pinholes in the spacer causing strong local ferromagnetic coupling. Furthermore, the interlayer exchange coupling energy exhibits a very strong dependence on temperature. The interlayer exchange coupling constant $J_{\text{exch}}$ shows a clear power-law dependence on magnetization, with an exponent that, at first sight, seems to depend on the EuS layer thickness. While no theoretical description is available that can be readily used to describe the finite temperature properties of this system, it is conjectured, along the line of reasoning proposed by Blinowski and Kacman [70], that the observed power-law dependence stems from a dependence of the interlayer exchange coupling energy on the exchange splitting of the bands in the two EuS layers.
Chapter 7

Magnetism of Gd-doped EuTe layers

In the introduction three topics in the investigation of spin filtering were mentioned: efficiency, magnetic separability and operating conditions. While the efficiency was already discussed in terms of magnetoresistance and the modification of magnetic switching fields was achieved by interlayer coupling, nothing was mentioned so far about the improvement of operating conditions of spin filters, as, for instance, imposed by their Curie temperature. This chapter discusses the addition of charge carriers to a magnetic semiconductor layer, which is expected to lead to a higher Curie temperature. For moderate doping levels the magnetic semiconductor has its Fermi level still inside its bandgap and can still be used as a spin filter, with a higher Curie temperature.

A second and perhaps more important reason for Gd doping is the possible occurrence of half-metallicity. It has been known for bulk materials that charge doping of a magnetic semiconductor can indeed create a half metal. At a certain doping level the Fermi level reaches the bottom of the conduction band and, if the conduction band is still exchange split, a half metal is formed. A half metal is a highly interesting source of spin polarization, both as a magnetic electrode in a magnetoresistance device, as well as for injection of a spin-polarized current into a semiconductor. This chapter describes the first results on an attempt to produce thin layers of a doped magnetic semiconductor that could be used in electrical devices.

7.1 Introduction

The still growing interest in the field of spintronics has already been mentioned at several occasions in this thesis, see for instance chapters 1 and 5. Several electronic applications based on the manipulation of the electron spin inside a semiconductor structure can be envisioned, that enable conversion of magnetic,
optical, and electrical signals into each other [7, 8, 141]. One of the challenges that have to be addressed for the development of such devices is the injection of a spin-polarized electron current into the semiconductor system. A current that is directly driven from a ferromagnetic metal into a nonmagnetic semiconductor (for instance in a magnetoresistance device) will not be highly spin polarized, due to the large impedance mismatch between the metal and the semiconductor [37], as was discussed in chapters 2 and 4.

One of the solutions, as was described in chapter 5, is injection of a spin-polarized current from a magnetic semiconductor (or a half metal) instead of a metal into the semiconductor system [36]. Injection of a spin-polarized current into a semiconductor was first demonstrated in 2000 for two different systems. Fiederling et al. [113] used a $n$-doped II-VI diluted magnetic semiconductor (DMS) as the source of a spin-polarized current. II-VI DMS are generally not ferromagnetic, but the application of a magnetic field causes their electron bands to spin split ($g$-factors up to 100), causing unequal carrier populations of spin-up and spin-down orientations in the conduction band. By applying a voltage a spin-polarized current is then led from the high-resistive DMS into a GaAs quantum well.

Ohno et al. [115] achieved spin injection in a similar experiment using a III-V DMS, GaMnAs, as the source of spin polarization. The main difference with the previous experiment is that GaMnAs is ferromagnetic at low temperatures (in this case $T_{C} = 50$ K), and thus has spin-split electron bands even at zero field, evading the necessity of large magnetic fields. At present, most of the research on injection of a spin-polarized current from a magnetic semiconductor into a nonmagnetic semiconductor has been based on GaMnAs [65, 117, 142].

All known ferromagnetic III-V DMS materials, like GaMnAs are $p$-type semiconductors. The II-VI semiconductor used by Fiederling et al. [113] is $n$-type, but it is not ferromagnetic. The spin relaxation time of electrons is in most practical semiconductor quantum wells (e.g., GaAs or CdTe) much larger than that of holes [143, 144]. It would therefore be desirable have a $n$-type ferromagnetic semiconductor available as the source of spin polarization. The family of Gd doped Eu chalcogenides (EuO, EuS, EuSe, and EuTe) would provide such a $n$-type ferromagnetic semiconductor.

It has been shown [145] that if a substantial amount of Eu atoms in a Eu chalcogenide is replaced with Gd, another interesting effect can occur. As a result of this $n$-type doping the Fermi level increases and, at a certain moment, it will reach the bottom of the exchange-split conduction band. It was predicted for Eu chalcogenides that in this case a half metal will form [145]. Half metals find their use both as magnetic electrodes in magnetoresistance devices, as well as for injection of a spin-polarized current into a semiconductor.

An additional advantage of ($n$-)doping magnetic semiconductors is an expected increase of their Curie temperatures, resulting from an additional (RKKY)
exchange interaction between the local magnetic moments, so-called carrier-induced magnetism [141]. The field of carrier-induced magnetism dates back to 1964, when Holtzberg et al. discovered that the electrical conductivity and the Curie temperature of Gd$_2$Se$_3$ increased dramatically upon the addition of a small excess of Gd [146]. In 1986, Story et al. reported on the induced ferromagnetism in the IV-VI semiconductor Pb$_{1-x-y}$Sn$_y$Mn$_x$Te by the addition of charge carriers [147]. A quantitative description of the effect was first obtained by Swagten et al. by a RKKY interaction that is mediated by holes from different points in the band structure of the material [148].

Carrier-induced magnetism gained a lot of momentum with the further investigation of the aforementioned III-V DMS semiconductors, where the ferromagnetism is induced by the $p$-type doping of the semiconductor with Mn. This interest was also fueled by predictions by Dietl of room-temperature ferromagnetism for certain compounds [141]. The enhancement was predicted to be especially effective for $p$-type doping. However, until now no ferromagnetism has yet been unambiguously demonstrated for such a semiconductor at room temperature.

The aforementioned Eu chalcogenides (EuO, EuS, EuSe, and EuTe) doped with Gd offer the opportunity to further study to which extend the Curie temperature can be enhanced by the addition of charge carriers. As was mentioned above they are all $n$-type. Regarding the choice of material from the four members of the Eu chalcogenides, Eu$_{1-x}$Gd$_x$S would be a logical choice, in view of the research directions described in the rest of this thesis. However, we chose Eu$_{1-x}$Gd$_x$Te, because it allows for epitaxial growth in combination with the well-known semiconductor CdTe. EuTe is an antiferromagnet and the Curie temperature that can at maximum be achieved for (bulk) Eu$_{1-x}$Gd$_x$Te [149] is lower than that of Eu$_{1-x}$Gd$_x$S [150]. Since for this study a model system is required, the disadvantage of the lower Curie temperature is compensated by the advantage of the possibility of combination with other well-known materials, like CdTe. As undoped EuTe itself is antiferromagnetic, for a demonstration of carrier-induced ferromagnetism it is thus sufficient to show the presence of ferromagnetic Eu$_{1-x}$Gd$_x$Te, without determining its precise Curie temperature.

The discovery of (antiferromagnetic) ordering in EuTe was reported simultaneously with that of ferromagnetic ordering in EuS, see also figure 1.2 [12–14]. EuTe is antiferromagnetic below its Néel temperature of 9.6 K, and it is paramagnetic at higher temperatures [151]. The effect of carrier-induced magnetism in EuTe by Gd doping was first demonstrated in 1966 by Holtzberg et al. [150]. They determined the paramagnetic Curie-Weiss and the ferromagnetic Curie temperature of bulk Eu$_{1-x}$Gd$_x$Te for the full range of compositions ($0 < x < 1$), as depicted in figure 7.1. In the region of “low” doping levels ($x < 0.1$) the antiferromagnetic state is transformed into a ferromagnetic state upon the addition of electrons by doping with Gd, which is ascribed to the RKKY interaction [59]. For Gd substitution of up the 60% of the cations the material remains ferromagnetic.
Figure 7.1: Paramagnetic Curie-Weiss temperature $\theta$ (black) and ferromagnetic Curie temperature $T_C$ (grey) as a function of the Gd concentration in Eu$_{1-x}$Gd$_x$Te according to Holtzberg et al. [150]. The Curie-Weiss temperature is based on an extrapolation of the magnetic susceptibility at high temperatures and can therefore assume values below 0 K (for instance for undoped EuTe), which is in fact an indication of antiferromagnetism.

However, for a higher Gd content Eu$_{1-x}$Gd$_x$Te becomes antiferromagnetic again, as a result of the shortening of the RKKY oscillation period with the carrier concentration, see also De Jonge et al. [152].

The addition of charge carriers to an intrinsic, magnetic semiconductor will not only modify its magnetic properties, but will also inevitably change the electrical behavior. By the addition of Gd donor states to the EuTe, initially the Fermi level will rise with respect to the conduction band. Soon an electron population will form in the conduction band and transport will be dominated by drift of electrons rather than by tunneling through the complete layer. At a certain doping level the Fermi level can reach the bottom of the conduction band. If it is exchange split this means that a half metal will be formed. For an even higher amount of dopants, electrons of both spin orientations should show metallic behavior.

This chapter reports on an exploratory study on the possibility to grow layered structures based on Eu$_{1-x}$Gd$_x$Te, in which the magnetic properties of undoped
EuTe are modified by Gd substitutional doping. The discussion is limited to the magnetic properties. It is expected that these results will initiate research regarding the electrical properties of such thin layers and the suitability for possible applications.

### 7.2 Magnetic properties of thin Gd-doped EuTe layers

A series of Eu$_{1-x}$Gd$_x$Te layers was grown at the Institute of Physics of the Polish Academy of Sciences by MBE from the separate constituents, as discussed in chapter 3. Freshly cleaved single-crystalline BaF$_2$ was used as the substrate. Either a EuTe or a PbTe layer was grown as a buffer layer between the substrate and the Eu$_{1-x}$Gd$_x$Te. Several of these samples showed ferromagnetism. The typical carrier concentration in the ferromagnetic Eu$_{1-x}$Gd$_x$Te layers was $10^{20}$ cm$^{-3}$, which corresponds to the substitution of about 1% of the Eu ions with Gd. With this amount of Gd doping the magnetism of the material is still described by the left part of the curve in figure 7.1, where the Curie temperature still increases with an increasing Gd content. Also layers with substantially lower carrier concentrations were grown. They did, however, generally not show ferromagnetism.

In this section the magnetic properties will be discussed of one specific ferromagnetic Eu$_{1-x}$Gd$_x$Te layer, where approximately 1% of the Eu atoms is replaced with Gd, that is typical for all ferromagnetic Eu$_{1-x}$Gd$_x$Te layers. The full sample structure is BaF$_2$(111)//PbTe(1000Å)/Eu$_{1-x}$Gd$_x$Te(2000Å), in which the layer thicknesses have not yet been determined exactly and contain an uncertainty of around 10%. The substrate temperature during growth was 380°C for this particular layer.

Figure 7.2 shows the magnetic hysteresis loop of this Eu$_{1-x}$Gd$_x$Te layer, measured along two different axes within the sample plane. A clear ferromagnetic behavior is observed with a coercive field of about 4 mT. The two hysteresis curves measured along the two different in-plane crystallographic orientations are similar, suggesting only a small anisotropy within the sample plane. On the other hand, shape anisotropy is of importance. The magnetic moment observed in out-of-plane measurements (not shown) is within the field range of figure 7.2 always below 50 nAm$^2$, indicative for an in-plane anisotropy. The inset of figure 7.2 shows the (inverse of the) paramagnetic susceptibility of a similar Eu$_{1-x}$Gd$_x$Te layer as a function of the temperature, measured at the Institute of Physics of the Polish Academy of Sciences in Warsaw [153]. The susceptibility diverges at 13-14 K, providing a first estimate of the Eu$_{1-x}$Gd$_x$Te Curie temperature.

The evolution of the Eu$_{1-x}$Gd$_x$Te hysteresis loops with temperature is depicted in figure 7.3 for the same sample. The observed behavior resembles what is
Figure 7.2: Hysteresis loops of a BaF$_2$(111)//PbTe/Eu$_{1-x}$Gd$_x$Te sample (x $\approx$ 0.01) at a temperature of 2 K, taken from a measurement between -0.1 T and 0.1 T. Loops measured along the [110] and [112] in-plane crystallographic axes are shown. The inset shows the temperature dependence of the paramagnetic susceptibility for a similar Eu$_{1-x}$Gd$_x$Te layer [153].

Figure 7.3: Hysteresis loops of a BaF$_2$(111)//PbTe/Eu$_{1-x}$Gd$_x$Te sample (x $\approx$ 0.01), measured along the [112] direction for a range of temperatures below and around the Eu$_{1-x}$Gd$_x$Te Curie temperature of 15 K.
expected for a ferromagnet. With an increasing measurement temperature a gradual decrease of both the magnetic moment and the coercivity of the Eu\(_{1-x}\)Gd\(_x\)Te layer is observed. Moreover, the strongest decrease of the magnetic moment occurs close to the expected Curie temperature. The coercive field appears to diminish mainly at a somewhat lower temperature. This might be related to the change of the magnetic anisotropy, but a more detailed study would be required to draw any conclusions.

In order to determine the Curie temperature of this Eu\(_{1-x}\)Gd\(_x\)Te layer more accurately, a so-called Arrot plot is drawn in figure 7.4. In an Arrot plot the square of the magnetization is plotted against the ratio of the applied field and the magnetization. It was shown by Arrot that these two quantities should be approximately linearly related for measurements at the Curie temperature [154]. From figure 7.4 it can be concluded that the Curie temperature of this Eu\(_{1-x}\)Gd\(_x\)Te layer is 15 ± 0.5 K, a value that is close to the paramagnetic Curie temperature that was derived from the inset of figure 7.2.

The magnetic moment of the sample was also measured at larger fields. Figure 7.5 shows the magnetic moment as a function of the magnetic field up to 5.5 T. As can be seen, the rapid ferromagnetic response at low fields, see also figure 7.2, of about 800-1000 nAm\(^2\) at 2 K is followed by a much slower increase to a saturation value that is not yet reached at 5.5 T. MOKE measurements on similar Eu\(_{1-x}\)Gd\(_x\)Te layers revealed saturation of the magnetization for fields higher
than 10 T. The initial rapid increase, followed by a much slower increase towards saturation, can be explained if the carriers are not evenly distributed over the EuTe. In that case, only certain regions will contain a substantial amount of carriers, locally leading to ferromagnetism. At the same time other regions in the Eu$_{1-x}$Gd$_x$Te will lack a sufficient amount of charge carriers to become ferromagnetic. Depending on the exact carrier density and on the temperature, these regions will be either paramagnetic or antiferromagnetic and therefore strong fields are needed to also completely magnetize these regions. The inhomogeneous carrier density can have three possible reasons: First of all, for weakly-doped systems it might be energetically favorable to separate in electron-rich and electron-poor regions, which is expected in manganites, and suggested in several DMS materials, see for instance the review by Nagaev [155]. A second explanation is the existence of Gd-rich and Gd-poor sublayers within the Eu$_{1-x}$Gd$_x$Te as a result of a varying flux during growth, leading to different doping levels. Third, a spread in carrier density could also be due to a random inhomogeneous distribution of Gd through the Eu$_{1-x}$Gd$_x$Te layer, as a result of a possible non-ideal growth (spontaneous phase separation into Gd rich and Gd poor regions). It has to be mentioned, however, that the last two possibilities are not supported by a strong broadening of the Eu$_{1-x}$Gd$_x$Te peak in X-ray diffraction measurements on similar Eu$_{1-x}$Gd$_x$Te layers [156].

**Figure 7.5:** Magnetic moment of a BaF$_2$(111)/PbTe/Eu$_{1-x}$Gd$_x$Te sample, where x $\approx$ 0.01, that was also used for the previous figures, measured as a function of the applied magnetic field at various temperatures.
7.3 Conclusion

In conclusion, it is possible to grow ferromagnetic Eu$_{1-x}$Gd$_x$Te thin films and thus to observe carrier-induced magnetism by $n$-type doping for this system. Several magnetic samples with a Curie temperature up to 15 K were produced. The magnetic behavior can be thought of as the sum of two effects. At relatively low fields ($< 0.1$ T) a hysteresis loop can be discerned that is associated with a magnetic moment of approximately half the value of the saturation magnetic moment. At higher fields a slow increase of the magnetization towards its saturation value can be observed, although saturation is not yet observed at 5.5 T, the highest field that was available. Measurements on similar samples have indeed shown that saturation of the magnetization only takes place for fields higher than 10 T [153]. The occurrence of two contributions to the magnetic moment could be explained by assuming that the charge carriers are not spread evenly over the Eu$_{1-x}$Gd$_x$Te layer. In that case the layer can be divided into a ferromagnetic part due to regions with a relatively high carrier concentration that saturates at a low magnetic field of the order of 10 mT, and an antiferromagnetic or paramagnetic part of regions lacking carriers that is not yet saturated at 5.5 T.

Further improvement of the growth has to lead to more homogenous magnetic properties. With the development of the Eu$_{1-x}$Gd$_x$Te layer growth, not only the magnetic, but also the electrical properties of the layer will have to be investigated. Only then it is possible to judge how Eu$_{1-x}$Gd$_x$Te can be used in spin-electronic devices.
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This thesis describes the results of a feasibility study on the use of the magnetic semiconductor europium sulfide (EuS) as a so-called “spin filter”. A spin filter is a tunnel barrier with a barrier height that depends on the spin orientation of the tunneling electron. A whole myriad of applications exists for such a layer, in particular in the field of spintronics. Spintronics is an extension of current electronics, in which not only the electron charge but also its spin is exploited. This allows for many new applications, such as nonvolatile fast memories and reprogrammable logic, which is a type of electronics that can change functionality if a magnetic field is applied. For many applications, however, it is necessary to inject a current that consists of unequal amounts of spin-up and spin-down electrons into a semiconductor. In order to create such a current, a high and spin-dependent resistance is needed. A spin filter meets these requirements and therefore constitutes a challenging, but highly interesting solution.

In this thesis several properties of spin filters will be treated that are of importance for their further development and implementation in electronics. An optimization study for a EuS spin filter tunnel barrier is presented and the magnetic properties of a spin filter will be discussed. Special attention is given to magnetic coupling effects: Both coupling between a spin filter and a neighboring magnetic electrode as well as coupling between two spin filter layers that are only separated by a thin nonmagnetic spacer layer are treated. Moreover, we will describe how a magnetoresistance resulting from two such spin filters, in a polarizer - analyzer fashion, depends on their resistance and on the spacer layer.

The thesis is organized as follows. First, chapter 2 addresses the theory that is at the basics of the physics that is described in this thesis. This chapter is followed by a brief description in chapter 3 of the experimental techniques that were used. In the subsequent chapters the aforementioned issues, regarding the application of EuS as a spin filter, are addressed.

Chapter 4 reports on the results of an optimization study on sputter-grown EuS tunnel barriers. Barriers grown at a temperature of 200°C and subsequently annealed at 400-450°C are best, both from magnetic and chemical point of view, as measured by SQUID an XPS, respectively. Combination of EuS as a tunnel barrier with a ferromagnetic electrode in principle leads to a magnetoresistance effect. Magnetoresistance is the dependence of the electrical resistance of a sys-
tem on an applied magnetic field. In this case the magnetoresistance is given by the relative change in resistance resulting from a change in the mutual alignment of the magnetizations of the two magnetic layers, which can be modified by the application of a magnetic field. For the practical realization of such a magnetoresistance device aluminum (Al) appears to be most suitable as a nonmagnetic bottom electrode and gadolinium (Gd) appears to be the best magnetic top electrode. This configuration allows for magnetoresistances of more than 100 percent. However, it is not possible to reliably produce such magnetoresistance devices, due to the roughness of the EuS layer. Other combinations of spin filtering EuS with a magnetic electrode only led to small resistance changes as a function of the applied magnetic field (<1%), of which the origin is not clear. It is therefore not possible to use sputter-grown EuS for the reliable fabrication of spin-filter structures.

Although the EuS spin filter is generally in direct contact with a ferromagnetic electrode (like Gd) for the systems mentioned above, it appears that the magnetic moment of both magnetic layers can be switched independently by application of a magnetic field. Chapter 4 also discusses the magnetic coupling between these two layers. Various detailed measurements show that the magnetic moments of EuS and Gd are weakly antiferromagnetically coupled to each other. The exact mechanism behind this coupling is not known. However, the interfaces of both materials can only be magnetized with very high magnetic fields, resulting in the presence of a nonmagnetic interface layer between EuS and Gd. This interface layer can in principle explain the absence of a strong direct coupling between the two magnetic layers.

In chapter 5 a proposal is presented to produce a magnetoresistance device based on two EuS spin filters, separated by a lead sulfide (PbS) spacer. The resistance of this system was determined within a two-current model, which means that a simple resistor model was used for electrons of each spin orientation separately. Such a calculation suggests that for realistic materials high magnetoresistance ratios (>100%) can be obtained, as long as the resistance of the spin filter layer is between one and one hundred times higher than that of the spacer layer.

The magnetic switching field of EuS can be adjusted by making use of magnetic interlayer coupling. The magnetic coupling between two EuS layers, separated by a nonmagnetic PbS layer, is discussed in chapter 6. In contrast to what is commonly observed in metallic structures, the coupling is always of antiferromagnetic nature in this semiconductor system. The magnetization of EuS was varied by performing measurements in a range of temperatures up to its Curie temperature. The interlayer coupling energy was found to depend strongly (as a fourth power) on the EuS magnetization. This is explained by the influence of the EuS magnetization on the band structure in the PbS spacer layer.

Finally, chapter 7 discusses the effect of the addition of charge carriers on the magnetic properties of a magnetic semiconductor. Europium telluride (EuTe), a
material that is chemically comparable to EuS, was $n$-doped with Gd (substitutional at Eu sites in the lattice). The originally antiferromagnetic EuTe becomes ferromagnetic upon the substitution of 1% of the Eu atoms with Gd, and can reach a Curie temperature of 15 K. This effect can be explained by magnetic coupling of the localized magnetic moments in the material to the free carriers that were added by the Gd doping. The investigated Gd-doped EuTe layers showed, apart from a ferromagnetic phase, also either a paramagnetic or an antiferromagnetic phase, probably due to a nonuniform distribution of the charge carriers in the layer, which could be an interesting subject for further research.
Samenvatting

Dit proefschrift bevat de beschrijving van de resultaten van een onderzoek naar de mogelijkheid van het gebruik van de magnetische halfgeleider europiumsulfide (EuS) als zogenaamd „spinfilter.” Een spinfilter is een tunnelbarrière, waarvan de barrièrehoogte afhankelijk is van de spinoriëntatie van het tunnelende elektron. Voor een dergelijke laag bestaat een heel scala van toepassingen, met name op het gebied van spintronica, de uitbreiding van de hedendaagse elektronica met het gebruik van de spin van het elektron. Dit opent de weg naar nieuwe functionaliteiten, zoals niet-vluchtige geheugens en elektronische schakelingen, waarvan de functionaliteit met behulp van magneetvelden veranderd kan worden. Voor veel toepassingen op dit gebied is het wél nodig een elektronenstroom van hoofdzakelijk één spinoriëntatie in een halfgeleider te injecteren. Voor het creëren van een elektronenstroom die uit ongelijke bijdragen van elektronen van beide spinoriëntaties bestaat is een hoge, spinafhankelijke weerstand nodig. Een spinfilter voldoet hieraan en is daarom een uitdagende, maar kansrijke oplossing.

In dit proefschrift wordt aandacht besteed aan verscheidene eigenschappen van een spinfilter die van belang zijn voor de verdere ontwikkeling en de implementatie in elektrische schakelingen. Zo wordt er een optimalisatiestudie voor een EuS spinfilterbarrière gepresenteerd en is er aandacht voor de magnetische eigenschappen van een spinfilter. In het bijzonder wordt aandacht besteed aan magnetische koppelingseffecten: zowel aan koppeling tussen een spinfilter en een naastgelegen magnetische elektrode als tussen twee spinfilters onderling die zijn gescheiden door een dunne tussenlaag. Daarnaast komt aan de orde hoe een magnetowerstand ten gevolge van twee zulke spinfilters, gebruikt als magnetische „polarisator” en „analysator,” afhangt van hun weerstand en van de tussenlaag.

Het proefschrift is als volgt opgebouwd. Allereerst geeft hoofdstuk 2 een inleiding in de theorie die aan de fysica beschreven in dit proefschrift ten grondslag ligt. Dit wordt gevolgd door een korte beschrijving van de experimentele technieken die zijn gebruikt (hoofdstuk 3). In de daaropvolgende hoofdstukken wordt dan ingegaan op bovengenoemde aspecten van het gebruik van EuS als spinfilter.

Allereerst is een optimalisatiestudie voor sputtergegroeide EuS tunnelbarrières uitgevoerd, waarvan de resultaten zijn weergegeven in hoofdstuk 4. EuS-barières die zijn gegroeid bij een temperatuur van 200°C en vervolgens geanneald bij 400-450°C, hebben de beste chemische en magnetische eigenschappen, zoals
die worden gemeten met respectievelijk XPS en SQUID. Combinatie van EuS als tunnelbarrière met een ferromagnetische elektrode zou in principe tot een magnetoweerstandseffect moeten leiden. Met magnetoweerstand bedoelt men de afhankelijkheid van de elektrische weerstand van een systeem van een aangelegd magneetveld. In dit geval gaat het om de relatieve weerstandsverandering ten gevolge van een verandering in de onderlinge oriëntatie van de magnetisaties van de twee magnetische lagen, die kan worden veranderd door toepassing van een extern magneetveld. Om een magnetoweerstandseffect te creëren blijkt aluminium (Al) het meest geschikt als niet-magnetische onderelektrode en gadolinium (Gd) als magnetische bovenelektrode. In deze configuratie kunnen magnetoweerstanden bereikt worden variërend van een paar tot meer dan 100 procent. Gebleken is dat het door de ruwheid van EuS niet mogelijk is op een betrouwbare manier dergelijke magnetoweerstandsdevices te produceren. Andere combinaties van spin-filterend EuS met een magnetische elektrode leidden slechts tot kleinere weerstandsveranderingen (≤1%) als functie van het aangelegde magneetveld, waarvan de oorzaak niet eenduidig valt af te leiden. Sputtergegroeid EuS kan dus niet worden gebruikt om op betrouwbare wijze spinfilterstructuren te produceren.

Alhoewel bij de bovenstaande structuren doorgaans een ferromagnetische elektrode, zoals Gd, in rechtstreeks contact is met het EuS spinfilter, lijken EuS en Gd als functie van het aangelegde magneetveld onafhankelijk van elkaar van magnetisatierichting te kunnen veranderen. Eveneens in hoofdstuk 4 is de magnetische koppeling tussen deze twee lagen onderzocht. Uit diverse, nauwkeurigere metingen blijkt dat EuS en Gd toch enigszins antiferromagnetisch aan elkaar gekoppeld zijn. Met andere woorden, hun magnetisatierichtingen zijn bij voorkeur tegengesteld aan elkaar. Het precieze mechanisme voor deze koppeling is niet bekend. Wel blijken de grensvlakken van beide materialen slechts met grote magneetvelden te magnetiseren, wat overeenkomt met het bestaan van een niet-magnetische grenslaag. Deze grenslaag lijkt in elk geval de afwezigheid van een zeer sterke, directe magnetische koppeling te verklaren.

In hoofdstuk 5 is een voorstel uitgewerkt voor een magnetoweerstandsdevice, gebaseerd op twee EuS spinfilters, gescheiden door een tussenlaag van loodsulfide (PbS). De weerstand van dit systeem is bepaald aan de hand van een twee-stromenmodel, waarbij voor elektronen van de beide spinoriëntaties apart een eenvoudig weerstandsmodel wordt doorgerekend. Uit een dergelijke berekening volgt dat voor realistische materiaalparameters hoge magnetoweerstanden (honderden procenten) mogelijk zijn, zolang de weerstand van het spinfilter tussen de één en honderd keer hoger is dan die van de tussenlaag.

Het magnetische schakelveld van EuS kan geregeld worden met behulp van magnetische interlaagkoppeling. De koppeling tussen twee EuS-lagen, gescheiden door een niet-magnetische laag PbS, is onderzocht in hoofdstuk 6. In tegenstelling tot hetgeen gangbaar is in metallische structuren, is de koppeling altijd antifer-
romagnetisch van aard in dit systeem van halfgeleiders. Door bij verschillende
temperaturen te meten, is de grootte van de magnetisatie van EuS gevarieerd.
De koppelingsenergie blijkt sterk (als een vierde macht) van deze magnetisatie
af te hangen. Dit wordt verklaard doordat de bandenstructuur in het PbS ook
wordt beïnvloed door de magnetisatie van het EuS.

Tenslotte is in hoofdstuk 7 het effect van het toevoegen van ladingsdragers op
de magnetische eigenschappen van een magnetische halfgeleider onderzocht. Eu-
ropiumtelluride (EuTe), een materiaal dat chemisch vergelijkbaar is met EuS, is
n-gedoteerd met Gd (substitutioneel op Eu roosterposities). Het van oorsprong
antiferromagnetische EuTe blijkt bij vervanging van 1% van de Eu ionen door
Gd ferromagnetisch te worden met een Curiemperatuur van 15 K. Dit effect
wordt verklaard met het magnetisch koppelen van de lokale magnetische mo-
menten in het materiaal aan de toegevoegde vrije ladingen. In de onderzochte
Gd-gedoteerde EuTe-lagen is naast de ferromagnetische ook een antiferromag-
netische of paramagnetische fase aanwezig, vermoedelijk door een niet-uniforme
verdeling van de ladingsdragers over de laag, hetgeen uitnodigt tot nader onder-
zoek.
List of publications

First author


Co-author


Dankwoord

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Curriculum Vitae

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