Molecular-Orbital Model of Heat-Induced Effective Exchange Coupling in Magnetic Multilayers

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of
Doctor of Natural Sciences

presented by

MICHAEL HUNZIKER
Dipl. Natw. ETH
born on April 14th, 1970
citizen of Kirchleerau, AG (Switzerland)

accepted on the recommendation of

Prof. Dr. H.-C. Siegmann, examiner
Prof. Dr. D. Pescia, co-examiner
Prof. Dr. M. Landolt, co-examiner

Zurich, June 2000
Er hob das Buch hoch und betrachtete es von allen Seiten. (…) Als er den Einband noch einmal genauer betrachtete, entdeckte er darauf zwei Schlangen, eine helle und eine dunkle, die sich gegenseitig in den Schwanz bissen und so ein Oval bildeten. Und in diesem Oval stand in eigentümlich verschlungenen Buchstaben der Titel: Die unendliche Geschichte.

Michael Ende

Im Andenken an meine Grossmutter
Liselotte Hunziker-Teschner
# Contents

Abstract  
2

Zusammenfassung  
4

1 Introduction  
6

2 Heat-Induced Exchange Coupling in Fe/ZnSe Multilayers  
9
  2.1 Introduction  
  9
  2.2 Experiment  
  9
  2.3 Results  
  11
  2.4 Discussion  
  13

3 Transport Measurements: Evidence for Interface Defect-States  
17
  3.1 Introduction  
  17
  3.2 Experiment  
  18
  3.3 Results  
  19
  3.4 Conclusions  
  24

4 The Molecular-Orbital Model  
27
  4.1 Introduction  
  27
  4.2 The Coupling Mechanism  
  28
  4.3 An Approximate Calculation  
  31
  4.4 Discussion  
  37
  4.5 Further Investigations  
  39

5 On the Way to Voltage-Controlled Exchange Coupling  
41
  5.1 Motivation  
  41
  5.2 Experimental Concept  
  42
  5.3 Results of Precursory Experiments  
  45

Bibliography  
47

Dank  
50

Curriculum Vitae  
51

Lebenslauf  
52
Heat-induced effective exchange coupling labels the antiferromagnetic coupling between thin ferromagnetic layers separated by an amorphous semiconductor spacer layer. Remarkably, this coupling exists at low temperatures and the coupling strength is found to increase reversibly with rising temperature. These two features are surprising because semiconductors at low temperatures do not provide any free electrons for the transmission of the coupling, and because magnetic effects in general tend to disappear upon heating.

Experimental data measured on the trilayer Fe/ZnSe/Fe are presented. The sign of the coupling is measured by Spin Polarized Secondary Electron Emission. We find antiferromagnetic coupling for spacers with thicknesses around 20 Å. For spacer thicknesses below this range, ferromagnetic coupling prevails while above weak or no coupling is observed. Magneto-Optical Kerr Effect allows to directly measure the coupling strength. The coupling strength $J$ is found to reversibly increase upon heating until it saturates at $T \approx 100$ K. There, its size is determined to be of the order of $J = 10^{-6}$Jm$^{-2}$. The described behavior is reversible for temperatures below $T \approx 200$ K; above, an irreversible transition takes place. The antiferromagnetic coupling is reduced and at around $T = 250$ K it finally disappears. This latter feature and the preparation conditions of the sample lead to the assumption that defects located at the interfaces are the key to the understanding of the coupling mechanism.

In order to give evidence to these interface defect-states, transport measurements are performed along bilayers consisting of Fe and ZnSe. We find zero conductivity for pure ZnSe layers. Thin Fe layers exhibit a finite conductivity with a semiconductor-like behavior. We conclude that Fe grows in grains distributed on the ZnSe surface. Bilayers evaporated at 30 K exhibit a sharp and large transition at $T \approx 250$ K. The behavior of this transition leads to the conclusion that localized electron states are present at the interfaces between Fe and ZnSe — electron states which irreversibly disappear at the transition temperature. Analyzing the data within the model of variable range hopping we find a density of defect states $N = 1 \times 10^{13}$eV$^{-1}$cm$^{-2}$. As a matter of fact, the transitions of the magnetic coupling in Fe/ZnSe/Fe trilayers on one hand and of the conductivity in Fe-ZnSe bilayers on the other occur at the same temperature. This strongly corroborates the conclusion that the coupling mechanism is based on the interaction of interface-defect states.
Consequently, a molecular-orbital model is devised in order to describe the coupling phenomenon. This model relies on defect states to be present at the two interfaces. The defects are assumed to be shallow donors which overlap across the spacer layer and form large "molecular-orbitals". Because of the Pauli principle the energies of these orbitals depend on the electron-spin configuration. This energy difference eventually drives the exchange coupling. As the energy of antiparallel spin configuration is lower than the one for parallel spins antiferromagnetic coupling prevails. The heat-induced behavior, however, is a consequence of thermal repopulation of the interfering donor states. The results of a approximate calculation, which is based on the molecular-orbital method, are found to very well agree with the experimental findings.
Zusammenfassung


Um die Existenz solcher Grenzschicht-Defekte zu beweisen, führen wir Transportmessungen an Doppelschichten aus Fe und ZnSe durch. Reine ZnSe-Schichten leiten überhaupt nicht. Eine dünne Fe-Schicht hingegen verhält sich wie ein amorpher Halbleiter. Wir schliessen daraus, dass Fe auf ZnSe als Verteilung von Fe-Gramulat wächst. An Fe-ZnSe-Doppelschichten, die bei 30 K erzeugt worden sind, finden wir bei T ≈ 250 K einen scharfen Übergang. Das Verhalten dieses Übergangs lässt sich mit der Existenz lokalisierter Elektronenzustände, welche sich an der Grenzschicht zwischen Fe und ZnSe befinden, erklären — Elektronenzustände, die bei der Übergangstemperatur irreversibel verschwinden. Eine quantitative Analyse dieser Daten mit dem Variable-Range-Hopping-Modell ergibt eine Defekt-Zustandsdichte von N = 1 \times 10^{13} eV^{-1} cm^{-2}. Es ist offen-
sichtlich, dass die magnetische Kopplung in Fe/ZnSe/Fe-Dreifachschichten bei derselben Temperatur verschwindet wie die Grenzschicht-Defekte in einer Fe-ZnSe-Doppelschicht. Diese Tatsache führt zum Schluss, dass die Wechselwirkung zwischen diesen Defektzuständen für das Auftreten der wärmeinduzierten Austauschkopplung verantwortlich ist.

Chapter 1

Introduction

In physics theoretical hypothesis and experimental evidence are related like two snakes biting in each other’s tail. It is of great advantage that theoretical concepts can be evidenced by experiments and experimental discoveries can be understood by theoretical models.

In solid state physics experiments must be performed on a phenomenological scale whereas theoretical models rely on quantum mechanical objects and their interactions. We study the interaction between two magnetizations which is a very familiar phenomenon on a macroscopic length scale. With quantum mechanics and the discovery of the electron spin as the smallest unity of magnetization [1] we have got a tool which allows us to understand the interaction between magnetizations microscopically.

The interaction between two magnetizations or, in words of quantum mechanics, a magnetic coupling is a manifold phenomenon to study:

A magnetic coupling is not only determined by its size, there is also an angle to be determined, as magnetizations may be described as vectors with size and direction. The phenomenological, effective coupling strength $J$ thus may be defined by the exchange energy of the interaction $E_{ex}$

$$E_{ex} = -J \frac{M_1 \cdot M_2}{|M_1||M_2|}$$

(1.1)

where $M_1$ and $M_2$ denote the two interacting magnetizations. A positive and negative sign of $J$ determines the magnetizations to stand parallel and antiparallel, respectively.

A magnetic coupling may either be mediated by a magnetostatic field or across electron wave-functions situated between the magnetizations. Of course, the mediation across electron states is the more interesting interaction. Surprisingly, it is of fairly long range and, with regard to theoretical understanding, it allows to study the behavior of electrons in solids.

The sign of the interaction across a free electron gas in general oscillates with increasing distance between the magnetic objects [2]. In the case of more than two
objects involved in a magnetic interaction, for example in a two or three dimensional lattice of magnetic clusters, the contributions to the interaction annihilate because of frustration. Therefore, a multilayer consisting of two dimensional ferromagnetic layers separated by non-ferromagnetic spacer layers is an ideal system to study magnetic coupling effects. In multilayers the ferromagnetic layers are separated by a well defined distance and therefore the direct contribution of the interaction remains.

In multilayers with metallic spacer layers such as Cr or Cu the magnetizations of the ferromagnetic layers were discovered to be coupled [3]. The sign of the interaction was found to oscillate with rising spacer thickness [4,5] while its size was observed to decrease amazingly slow. The mechanism of this coupling effect could be understood based on quantum mechanics and the electron spin: The interaction across the spacer layer is explained to be mediated by the gas of free electrons, either by a spin dependent confinement of the free electrons between the ferromagnetic layers [6] or by a RKKY type interaction [7,8]. Finally the two explanations resulted to be equivalent.

Multilayers with amorphous, semiconducting spacer layers evaporated at low temperatures were also found to be exchange coupled [9]. Mainly, at spacer thicknesses in the range of about 20 Å antiferromagnetic coupling is observed—with the most remarkable property that the coupling strength increases reversibly with rising temperature [10]. Therefore, this coupling was labeled “heat-induced exchange”. It could be observed so far for the spacer materials Si [9,10], Ge [11] and, as presented in this thesis, for ZnSe [12].

While the coupling mechanism in multilayers with metallic spacers could be explained in a simple and therefore convincing manner the mediation of the coupling across amorphous semiconductors remained an open question. As heat-induced exchange coupling can be observed even at low temperatures where no free electrons are present in the semiconductor it becomes clear that a new theoretical concept is needed in order to understand the coupling mechanism.

Briner in his considerations very early relied on defects in the semiconductor material [13], Walser later suspected the relation of defects with the interfaces [14]. In this thesis we present transport measurements along Fe/ZnSe interfaces which give strong evidence that the exchange coupling is mediated by localized electron states near or at the interfaces between semiconductor and ferromagnet [15]. The existence of these donor states is the key to the understanding of the coupling mechanism. Therefore, we introduce a model which relies on shallow donor states near the interfaces which interfere across the spacer layer and thus transmit the exchange coupling [16]. The concept of this coupling mechanism is completely new in magnetism. However, the interaction between the electron spins is quite analogue to the spin interaction in hydrogen molecules. Therefore, we name this concept the “molecular-orbital model”. The results of a roughly approximated calculation which is based on this model are found to very well agree with the experimental data and to be robust upon variation of the few free parameters.
In this thesis we close a circle. In a first step we present the experimental characterization of a puzzling effect in magnetism, the heat-induced effective exchange coupling. In a second step the key objects which make this effect running, the interface defect-states, are identified. Third, based on these key objects, we devise the molecular-orbital model, and forth we describe the model mathematically with reasonable accuracy. The circle closes quite properly as the experimental data are reproduced amazingly well by the calculation.

Closed circles demand new challenges. There remains the question of the technical applicability of magnetic coupling effects. The resistivity of magnetic multilayers is found to depend considerably on the alignment of the magnetizations, an effect which was labeled “giant magneto-resistance” (GMR) [17, 18]. The alignment of the magnetizations therefore can electronically be detected which allows to “read” binary information monitoring the resistivity of ferromagnetic multilayers. For storage also a “writing” process is needed. So far, the switching of magnetic alignment triggered by a current across the multilayer is known to require giant current densities [19]. In this thesis we present an influence of temperature on magnetic alignment in ferromagnetic multilayers with semiconductor spacers. This motivates to apply a voltage across the multilayers since voltage-controlled exchange coupling is of basic interest, with or without technical potential.
Chapter 2

Heat-Induced Exchange Coupling in Fe/ZnSe Multilayers

2.1 Introduction

Heat-induced exchange coupling is a magnetic interaction of which the coupling strength reversibly increases with rising temperature. As mentioned in the previous chapter, this coupling has been found for the amorphous spacer materials Si and Ge under the condition that the multilayers were prepared at temperatures around 30 K. In this chapter, we present measurements on amorphous Fe/ZnSe/Fe trilayers which yield a heat-induced exchange coupling as well. ZnSe is a compound material with ionic bindings and with a much larger energy gap than the one of covalent Si and Ge. Therefore it becomes clear that this coupling effect does not depend on a specific spacer material, it rather can be considered as a general magnetic behavior of ferromagnet-semiconductor multilayers. While Si and Ge react very easily with Fe, which has been used for the ferromagnetic layers in all previous and present measurements, Fe and ZnSe very poorly intermix even at room temperature [20]. Nevertheless, low temperature also is a preparation condition for the occurrence of the exchange coupling in Fe/ZnSe multilayers. We thus have got an indication that low temperature is decisive and not only inhibits the chemical reaction at the interfaces.

2.2 Experiment

The measurements are performed on a trilayer of amorphous Fe/ZnSe/Fe which is evaporated onto a crystalline Cu substrate. The amorphicity of the layers is checked by Low Energy Electron Diffraction (LEED). As we apply surface sensitive methods the magnetization of the bottom ferromagnetic layer needs to be well known during the measurement. It needs to be a “magnetic driver”, a layer with a hard magnetization of which the direction is well defined. Therefore, a
Chapter 2. Heat-Induced Exchange Coupling in Fe/ZnSe Multilayers

A thick and crystalline Co layer is placed between the substrate and the bottom Fe layer in order to make the magnetization of the bottom layer hard and to give it a well defined anisotropy. In detail, we first evaporate 70 Å Co onto the Cu substrate. An elevated temperature of about 90°C during the evaporation improves the crystalline anisotropy and enlarges the coercivity of the magnetization. 6 Å Fe complete the bottom ferromagnetic driver. The ZnSe spacer layer with variable thickness is evaporated at room temperature while we cool to 30 K for the completion to the sample with 15 Å Fe. We note that it is crucial to produce the top Fe layer at temperatures below 150 K in order to make the coupling occur. Further, low temperature during the ZnSe evaporation and a brief annealing at 150 K after completion of the multilayer favor the coupling effect. We assume that low temperatures support a smooth growth of the layers and hence flat interfaces are produced. The annealing softens the top layers magnetization and therefore makes it independent of pinnings at defects and edges.

ZnSe is evaporated from powder (Alfa, 99.999 %) in W crucibles whereas Fe (Alfa, 99.9985 %) and Co (Alfa, 99.9975 %) are evaporated from a rod. The evaporation rate is kept at about 2 Å/min. ZnSe evaporated onto a sapphire surface below 70°C is reported to grow amorphously; crystallization is to be expected at 170°C to 210°C [21]. The sample preparation as well as the measurements are performed in an ultra high vacuum (UHV) chamber with base pressure below $1 \times 10^{-10}$ mbar. The cleanliness of the sample is checked by standard Auger Electron Spectroscopy (AES). Within the resolving power of AES we do not find any interdiffusion to occur.

We use Spin Polarized Secondary Electron Emission (SPSEE) in order to probe the angle of the coupling depending on the spacer thickness. A 1–5 keV unpolarized electron beam produces a cascade of secondary electrons on the sample surface. The two in-plane components of the spin polarization $P$ are measured in a Mott detector. $P$ is proportional to the magnetization of the surface [22, 23], with the two components defined as $P_i = (N_i^\uparrow - N_i^\downarrow)/(N_i^\uparrow + N_i^\downarrow)$, where $N_i^\uparrow$ and $N_i^\downarrow$ are the number of electrons with spin parallel and antiparallel to the chosen quantization axis $i = x, y$, respectively. Hence, we monitor the magnetization of the top Fe layer and, as the bottom ferromagnetic layer is hard with a well defined anisotropy, we can determine the angle between the magnetizations. With the knowledge of the magnetizations direction we may apply Magneto-Optical Kerr Effect (MOKE) in order to determine the coupling strength $J$. A laser beam of linearly polarized light is reflected on the sample. The polarization of the reflected beam rotates due to the magnetization of the sample surface. MOKE is less surface sensitive than SPSEE what allows to study the magnetizations of the top and the bottom ferromagnetic layer at the same time. The $M(H)$-response depicted in Fig. 2.1 represents a typical MOKE measurement on a Fe/ZnSe/Fe/Co multilayer. The horizontal shift between the major hysteresis loop originating from the bottom layer and the minor loops originating from the top layer is identified as the compensation field $H_{comp}$. 
\( H_{\text{comp}} \) compensates the coupling strength \( J \), as defined in Eq. 1.1, and therefore is directly proportional to \( J \):

\[
J = t_{Fe} M_S H_{\text{comp}} \tag{2.1}
\]

\( t_{Fe} \) and \( M_S \) are the thickness of the top Fe layer and its saturation magnetization, respectively. This equation can easily be derived; at \( H_{\text{comp}} \) the magnetostatic energy of the top Fe layer \( E_{\text{stat}} = V_{Fe} M_S H_{\text{comp}} \) compensates the coupling energy \( E_{\text{coup}} = J A_{Fe} \), where \( V_{Fe} \) and \( A_{Fe} \) denote the volume and the area of the top Fe layer, respectively.

\section*{2.3 Results}

First we address the couplings dependence on the spacer thickness. To do so we evaporate a wedge-shaped ZnSe layer with a thickness between 6 Å and 28 Å. The surface magnetization is monitored along the wedge measuring the spin polarization at remanence by SPSEE. As shown in Fig. 2.2 we find a thickness range around 20 Å where the sign of the polarization is negative, above and below a positive sign prevails. The sign of the polarization not necessarily corresponds with the sign of the coupling. While negative polarization (antiparallel alignment of the magnetizations) always stands for antiferromagnetic coupling, positive polarization (parallel alignment) is ambiguous; it may stand for ferromagnetic or zero coupling. MOKE measurements yield strong ferromagnetic coupling at small spacer thicknesses while weak or zero coupling is found at large spacer thicknesses. Already these data give first evidence for a spectacular temperature behavior: The thickness range where antiferromagnetic coupling occurs broadens reversibly with rising temperature, mainly towards larger spacer thicknesses. Or, focusing on a fixed spacer thickness of about 24 Å, the antiferromagnetic coupling may be switched on and off by temperature.

Measuring the coupling strength in the “switching” thickness range we observe this heat-induced temperature behavior more accurately. As shown in Fig. 2.3, MOKE measurements reveal the coupling strength to increase upon heating until
Chapter 2. Heat-Induced Exchange Coupling in Fe/ZnSe Multilayers

Figure 2.2: Spin polarization $P$ of secondary electrons at remanence of the top Fe layer of an Fe/α-ZnSe(wedge)/Fe sample deposited on a 70 Å Co/Cu(100) substrate, versus ZnSe spacer thickness. In-plane components parallel and perpendicular to the magnetizing field are shown. The change between the behavior at 40 K and at 150 K is fully reversible.

It saturates. We emphasize that this behavior is strictly reversible. Considering the temperature behavior for different spacer thicknesses with ascending order one observes a decay of the coupling strength at thermal saturation. At a spacer thickness of 30 Å a reversible switching from ferromagnetic coupling at 20 K to antiferromagnetic coupling above 50 K can be found. We measure $H_{\text{comp}}$ and derive $J$ with Eq. 2.1. The magnitude of $J$ is found to be small, it lies in the range of $10^{-6}$ Jm$^{-2}$.

A careful look at the data of the polarization measurements and the data of the coupling strength measured by MOKE reveals that they are not perfectly consistent. We attribute this to the fact that the MOKE measurements have been recorded later in the course of the experiments. The thickness range where antiferromagnetic coupling occurs is found to slightly shift with the lifetime of the ZnSe evaporators.

An important information for the discussion of the coupling mechanism is the temperature where the above described phenomenon disappears. The reversibility of the couplings temperature behavior is restricted to temperatures below 200 K. Above, an irreversible transition takes place, compare Fig. 2.4. The neg-
2.4 Discussion

The multilayer Fe/ZnSe/Fe/Co is a very suitable sample to characterize heat-induced exchange coupling. The remanent and soft magnetization of the top Fe layer and the hard magnetization of the magnetic driver allow a direct and accurate measurement of the coupling strength \( J \). Remarkably, the sample exhibits the exchange coupling despite of its spacer layer which is almost insulating. Moreover, the coupling persists even at 40 K. The MOKE measurements allow to determine the temperature dependence of \( J \). The characteristic behavior with an increasing size of \( J \) below 100 K and a saturation above is a suitable touchstone for the results of theoretical models.

Figure 2.3: Coupling strength \( J \) versus temperature for a variety of spacer thicknesses. We measure \( H_{\text{comp}} \) by MOKE and derive \( J \) with Eq. 2.1. In the temperature range chosen, all temperature dependences are fully reversible. We note that the coupling of samples with larger spacer thicknesses undergoes a sign change. The error bars originate from the quality of the minor loops.

The positive sign of the coupling disappears and ferromagnetic coupling prevails which hardly depends on temperature.
The irreversible transition measured at about 250 K is another characteristic behavior which helps to unveil the coupling mechanism. We know that Fe and ZnSe are chemically inert which is supported by the fact that the remanent magnetization of the top Fe layer survives the transition. Therefore, the occurrence of the transition gives strong evidence that small structural changes may destroy the coupling phenomenon. The fact that the transition takes place at 250 K while the whole multilayer except the top Fe layer has been evaporated at room temperature gives an indication that these structural changes occur at the interfaces between ZnSe and Fe. One might think of defect states at the interfaces to be involved with the coupling mechanism. Their existence would agree with the experimental observations.

In order to discuss the coupling phenomenon more generally we compare the present data with the data measured on multilayers with Si [9, 10] and Ge [11] spacers. First of all, the antiferromagnetic coupling occurs across all mentioned spacer materials in the same range of spacer thickness, compare Fig. 2.5. We note that the thickness range does not depend on the size of the semiconductors energy gap, rather a dependence on the dielectric constant \(\varepsilon\) may be observed.

The measurements on multilayers with Ge spacers revealed the necessity of an annealing at 190 K in order to make the coupling occur. This observation already gave rise to the suspicion that the interfaces play an im-
important role for the mediation of the coupling [14]. Furthermore, at that point of investigation it was questioned whether the ferromagnetic layers were separated by a pure semiconductor layer or if rather a compound layer was formed, due to the reactivity between Fe/Si and Fe/Ge, respectively. Therefore, X-Ray Photoelectron Spectroscopy (XPS) measurements were performed on Fe/Si and Fe/Ge heterostructures in order to examine the layer structure and the chemical interface properties [25]. During preparation of the sample and measurement the temperature was kept low such that the conditions were similar to the ones of the coupling experiments. Between the Fe layer and the Si (Ge) substrate a compound layer of homogeneous composition was detected while a Si (Ge) layer on top of a Fe substrate could not be observed to intermix with the substrate. The thickness of the compound layer at the Fe/Si (Fe/Ge) interface at 30 K is low enough such that in trilayers, where the coupling has been observed, the ferromagnetic layers still are separated by a pure semiconductor. Obviously, the thickness of the pure spacer layer is reduced compared to its nominal value. Finally, the resolving power of XPS was too low to observe any change of the interface properties while annealing.

The properties of the coupling effect as well as the preparation conditions of the sample do not unambiguously reveal the coupling mechanism. However, some concepts can be excluded; let us cut the weeds before we dig for the diamonds. All attempts to explain the mediation of heat-induced exchange coupling by free electrons should be abandoned because of the occurrence of the coupling at low temperatures and because of the lack of a

Figure 2.5: Compilation of the spacer-thickness dependence of the surface polarization in multilayers with Ge, Si and ZnSe spacers (from Refs. [11], [9] and [12]). The thickness range of antiferromagnetic coupling follows more the dielectric constant of the semiconductor ($\varepsilon_{Ge} = 16$, $\varepsilon_{Si} = 11.2$, $\varepsilon_{ZnSe} = 9.2$) than the semiconductors energy gap ($\Delta E_{Ge} = 0.67$ eV, $\Delta E_{Si} = 1.1$ eV, $\Delta E_{ZnSe} = 2.6$ eV) [24].
dependence on the size of the semiconductors energy gap. Moreover, free electrons would not be sensitive to small structural changes and therefore no irreversible transition would be observed. “Metal-induced gap states”, free electrons which leak from the Fe into the semiconductor, would not be annihilated by such structural changes either. Further, magnetostatic interactions can be excluded because they do not reversibly exhibit a heat-induced behavior. So far, the mediation via defect states remains the only explanation. An evidence for such defect states and the coupling mechanism will be unveiled in the course of this study.
Chapter 3

Transport Measurements: Evidence for Interface Defect-States

3.1 Introduction

The behavior of the magnetic coupling phenomenon gives rise to the assumption of defect states to be the key to the understanding of the coupling mechanism. Assumption is not evidence and in order to understand the interaction, the location, the density and the relative position on the energy scale of the defect states are needed to be known.

In order to answer these questions we present transport measurements which have been performed along bilayers consisting of one ferromagnetic metal layer and one amorphous semiconductor layer. In amorphous semiconductors with the Fermi energy $E_F$ lying in the range of localized defect states, the conduction may be described by two different mechanisms [26]. First, the current may evolve across the defect states by variable range hopping and second, electrons may be excited into the conduction band and establish a current carried by free electrons. The energy gap between the conduction band edge $E_C$ and the center of the defect levels $E_S$ ($\sim E_F$ in our case) even for shallow donors is in the range of 10 meV. Therefore, at low temperatures the conductivity depends on $N(E_F)$, the density of the defect states at the Fermi level, while at higher temperatures the energy gap $E_C - E_F$ rules the current.

In heterostructures the influence of the neighboring metallic layers on the formation of interface defect-states can not be neglected. The specific conductivity of these metal layers is enormous compared to the one of semiconductors, specially at low temperatures. In order to measure the contribution of the semiconductors to the total current of a metal-semiconductor heterostructure we hold the thickness of the metal layers in the range of a few monolayers. For a first
Chapter 3. Transport Measurements: Evidence for Interface Defect-States

approximation, the conductivity of percolated metal layers $\sigma_m$ is assumed not to depend on temperature.

For a mathematical description of the mentioned conductivities we follow the considerations of Mott and Davis [26]. They describe variable range hopping in non-crystalline semiconductors. The conductivity for a hopping current in a three dimensional semiconductor is given by

$$\sigma_{3D}(T) = \sigma_{0,3D}(T) \exp(B_{3D}T^{-1/4})$$  \hspace{1cm} (3.1)

where $\sigma_{0,3D} = 2e^2N(E_F)R^2\nu_{ph}$ and $B_{3D} = (24\alpha^3)/(\pi N(E_F)k)^{1/4}$. 

$R = (3/2)^{1/4}(\pi \alpha N(E_F)kT)^{-1/4}$ is the mean hopping distance, $\nu_{ph}$ the electron-phonon interaction constant and $\alpha$ the decay constant of the localized states. For a two dimensional current evolving in thin layers or along surfaces and interfaces Eq. 3.1 is slightly altered

$$\sigma_{2D}(T) = \sigma_{0,2D}(T) \exp(B_{2D}T^{-1/3})$$  \hspace{1cm} (3.2)

with $\sigma_{0,2D} = 2e^2N(E_F)R^2\nu_{ph}$, $B_{2D} = (28\alpha^3)/(9\pi N(E_F)k)^{1/3}$, and $R = (3/2)(\pi \alpha N(E_F)kT)^{-1/3}$.

The conductivity caused by free electrons which are thermally excited from defect states follows the familiar excitation law

$$\sigma_{exc}(T) = C \exp(-\frac{E_G - E_F}{kT})$$  \hspace{1cm} (3.3)

where $C$ is a parameter which depends on the details of the electronic structure and the mean free path.

3.2 Experiment

We perform our measurements on a sapphire substrate as depicted in Fig. 3.1. The sapphire surface is cleaned by sputtering with Ar. Onto this surface two Au electrodes are evaporated which are divided by a gap of 3 mm width and 30 µm length. The Au electrodes are contacted by thin Cu wires. The sapphire is fixed onto a Cu block for temperature control in the range of 20 K to 450 K. The temperature is measured by a cromel-alumel thermoelement.

For the semiconductor layer we use ZnSe, for the metal layers Fe or Co are used. As mentioned, Fe and ZnSe as well as Co and ZnSe are known to poorly intermix at the interfaces [20, 27] and to not produce any compound layers with
particular electronic properties. In order to achieve thin layers with a similar consistency as produced for the coupling experiments we work at UHV conditions and we grow the heterostructures the same way, by molecular beam epitaxy onto the substrate surface held at 30 K. For the details see section 2.2.

As we are investigating metastable structures it is of decisive importance to clearly distinguish between reversible and irreversible thermal behavior. Therefore, in order to properly analyze the temperature dependences we introduce an annealing temperature \( T_i \). We heat the sample up to \( T_i \) and measure the temperature dependence of the conductivity with decreasing temperature, “freezing” the sample. In order to vary \( T_i \) we run heating and cooling cycles of conductivity measurements where the annealing temperature increases on each cycle. Since the bilayer samples are very inhomogeneous by definition we work with the absolute conductivity instead of the specific one.

3.3 Results

In bilayers, a current may run along the bottom layer, the top layer, along the interface or along a combination of all the three. Therefore, in order to determine the contributions to the current of the present measurement, we first examine the different layers separately.

A pure ZnSe layer of 150 Å thickness evaporated at 30 K is found to be completely insulating at all temperatures up to 450 K, i.e., the conductivity is measured to be below \( 10^{-11} \Omega^{-1} \) which is our detection limit; compare Fig. 3.2, full dots.

A pure Fe layer of 4 Å thickness evaporated at 30 K on top of the sapphire substrate exhibits a measurable conductivity; see Fig. 3.2, empty dots. The conductivity behaves like an amorphous, two dimensional semiconductor — the data can be fitted by Eq. 3.2 quite accurately. Assuming \( \alpha^{-1} = 10 \, \text{Å} \), which is here somewhat arbitrary, we find \( N(E_F) = 2.5 \times 10^{12} \text{eV}^{-1}\text{cm}^{-2} \) to remain constant upon annealing.

In order to examine the interface properties between Fe and ZnSe we study bilayers of three configurations. First, a thin Fe layer on top of a ZnSe bottom layer (4 Å Fe / 130 Å ZnSe), second, a thicker Fe layer on ZnSe (18 Å Fe / 150 Å ZnSe), and third, an inverse bilayer consisting of a thin Fe layer covered by ZnSe (60 Å ZnSe / 12 Å Fe). The results are given in Fig. 3.3, upper, center and bottom panels, respectively.

The measurements provide manifold results. First, we analyze what happens to a thin Fe layer on top of ZnSe, as shown in the top panel. We start at 30 K with zero conductivity. At all temperatures the conductivity behaves strictly like an amorphous, two dimensional semiconductor. While at low temperatures the conduction slightly decreases upon annealing, a sharp and large transition reduces the conductivity at 250 K. Above, a rather moderate annealing continues.
Figure 3.2: Conductivity vs temperature of 150 Å ZnSe (full dots) and 4 Å Fe (empty dots). In two separate experiments the layers are evaporated at 30 K onto a sapphire substrate. The measurement on the Fe layer are performed by stepwise annealing, the course of the experiment is indicated by arrows. The full lines are best fits according to Eq. 3.2.

In contrast, the thicker Fe layer (center panel) starts at 30 K with a finite conductivity. At low temperatures a semiconductor-like behavior is found after subtraction of a constant value of $\sigma_m = 5 \times 10^{-2}\Omega^{-1}$. However, no annealing process is visible. At 250 K an irreversible transition occurs as well, but this transition sharply enhances the conductivity. After the transition the temperature coefficient of the conductivity is negative and now an annealing process takes place.

Finally, the inverse bilayer with a thin Fe bottom layer (bottom panel) behaves quite similar to the bilayer with the thin Fe layer on top. The impact of the annealing at low temperatures is smaller, as well as the one of the transition at 250 K. After the transition no further annealing is observed until at around 450 K where crystallization processes of ZnSe start to play a role. During the evaporation process of this particular layer a truly remarkable feature may be observed: The coverage of the ground Fe layer by ZnSe enhances the conductivity by three orders of magnitude, even if ZnSe on its own has been measured to be insulating. We state that in all measurements the data do hardly depend on the thickness of the ZnSe layers.
3.3. Results

Figure 3.3: Conductivity vs. temperature measured along bilayers consisting of ZnSe and Fe vaporized at 30 K. The samples are stepwise annealed. The course of the measurement is indicated by arrows.

Bottom panel: inverse bilayer, 60 Å ZnSe on 12 Å Fe layer. Center panel: 18 Å Fe layer on 150 Å ZnSe. Top panel: 4 Å Fe layer on 130 Å ZnSe. The arrows are stepwise annealed.
The transition measured at 250 K, which occurs for all measured Fe-ZnSe bilayers, is the most remarkable result, of course. In order to get more information about the origin of this transition we alter the bilayer: First, we roughen the interface of a Fe/ZnSe bilayer and second, we study bilayers with Co replacing Fe.

In order to produce a bilayer with a rough interface, 155 Å ZnSe are sputtered with Ar for a few seconds at 2 kV. Then the sample is completed by 18 Å Fe. The data of the conductivity measured on this sample are given in Fig. 3.4 by empty dots. For comparison, the data measured on the same but unsputtered sample, already presented in Fig. 3.3, center panel, are given again by full dots. The results of this measurement reveal that the transition temperature strongly depends on the roughness of the interface. The transition of the rough sample is shifted to about 350 K. Furthermore, $\sigma_m$ is reduced and the temperature dependence of the conductivity is less pronounced.
Finally we perform measurements on Co/ZnSe bilayers. Analogue to the measurements on Fe/ZnSe we evaporate a 4 Å and an 18 Å thick Co layer on top of ZnSe holding the sample at 30 K in each case. The results, which are shown in Fig. 3.5, reveal a slightly different behavior compared to the data measured on Fe/ZnSe. On one hand, already 4 Å Co (upper panel) provoke a non-zero conductivity at low temperature. On the other hand the conductivity for 18 Å Co (lower panel) yields a negative temperature coefficient already for an as-grown sample. However, both samples undergo a transition at 250 K, with decreasing conductivity in the case of a thin Co layer and increasing conductivity for 18 Å Co.
3.4 Conclusions

In a heterostructure consisting of two well separated layers the current may propagate along three channels: Along one of the two layers and along the interface. In the case of Fe-ZnSe bilayers the contribution of the ZnSe layer to this propagation is found to be zero, even at room temperature. This result agrees with the measurements on amorphous ZnSe performed by Lim and Brodie [21]. They found for samples, which were annealed at 140°C, a density of defect states of about $N(E_F) \sim 10^{17} \text{eV}^{-1} \text{cm}^{-3}$. This translates in the case of a thin film of 130 Å thickness to $N(E_F) \sim 10^{11} \text{eV}^{-1} \text{cm}^{-2}$. The conclusion is simple: The energy gap of ZnSe is too large and its density of defect states is too low such as a measurable current could be established.

The conductivity of a thin Fe layer on top of the sapphire substrate behaves like an amorphous, twodimensional semiconductor. The current thus must propagate along the Fe layer hopping from one site to another. Therefore we conclude that Fe on top of the sapphire surface grows in a distribution of grains. As the conductivity of a Fe/ZnSe bilayer reveals a similar behavior, Fe on top of ZnSe must grow similarly. Thin Fe layers exhibit zero conductivity towards 0 K which indicates that the grains are well separated from each other. Further, the slight reduction of the conductivity upon annealing may be attributed to a contraction of the Fe grains which also widens the gaps in between. Finally, thicker Fe layers or Co layers on a ZnSe bottom layer exhibit a semiconductor-like conductivity after subtraction of a “metallic” offset $\sigma_m$. In this case the growth still yields grains, however, they are connected among each other.

The large irreversible transition measured on Fe-ZnSe bilayers is the most remarkable result of these measurements. This transition occurs neither in pure ZnSe layers nor in pure Fe layers, compare Fig. 3.2. Therefore we conclude that the origin of this transition is located at the interface. Possible coagulation effects, which could dramatically contract the Fe grains and thus reduce the conductivity, can be excluded. The reason is the occurrence of the transition in inverse bilayers where the Fe grains are covered by ZnSe and therefore have no degrees of freedom for a dramatic deformation. Furthermore, at 250 K no intermixing between Fe and ZnSe is expected.

The origin of the transition is unveiled by the behavior of the conductivity: In the case of samples with thin Fe layers the transition leads to a reduction of the conductivity whereas on samples with thicker Fe layers the conductivity is sharply enhanced. We conclude that at temperatures below the transition localized electron states are present at the interface between Fe and ZnSe which disappear upon annealing at 250 K. In the case of thin Fe layers where the Fe grains are disconnected and the conductivity is in the hopping regime these states provide additional hopping sites. The conductivity is reduced when they disappear. In the case of thicker Fe layers where the Fe grains are connected and band electrons dominate the conductivity these localized states may act as traps
and scatter the free electrons. Thus a reduction of these traps enhances the total conductivity.

These conclusions are supported by a quantitative analysis of the data. We fit the data with Eq. 3.2, where we set $\alpha^{-1} = 10 \text{ Å}$, which has been found to be appropriate for defects in amorphous Si [26] and which in our case is assumed to not alter upon annealing. The results are given in Tab. 3.1. For the thin Fe layers (top and bottom panels) best fits before and after the transition are available. The density of defect states which is lost by the transition is about $\Delta N(E_F) \approx 1 \times 10^{14} \text{eV}^{-1}\text{cm}^{-2}$. We neglect the complexity of a granular interface and shall take this value as an approximative measure of the density of defect states at Fe-ZnSe interfaces.

Finally, we state that a Fe induced band bending in the ZnSe layer does not exhibit a mayor influence on the conductivity. Because of the low defect concentration in ZnSe the bending would be of long range. However, the conductivity does not depend on the thickness of the ZnSe layer.

The coincidence of the transition temperatures of magnetic and transport measurements on Fe-ZnSe multilayers is obvious. Since the layers are produced the same way in both experiments it is conclusive that these transitions have the same origin. On one hand this transition makes the heat-induced antiferromagnetic coupling disappear, on the other hand it annihilates localized electron states at the interfaces. Therefore we conclude that interface defect-states are responsible for the exchange coupling.

While the existence, location and density of the defect states could be identified their relative position on the energy scale remains an open question. The present data do not include a contribution of free electron conduction, compare Eq. 3.3, which would determine $E_C - E_S$. Either this energy gap is too large or the parameter $C$ is too small such as a contribution by free electron conduction could be measured. Therefore, alternative methods like photoemission should be applied.

<table>
<thead>
<tr>
<th>$T_i$ [K]</th>
<th>$N(E_F)$ [eV$^{-1}$ cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>$3.3 \cdot 10^{13}$</td>
</tr>
<tr>
<td>150</td>
<td>$3.5 \cdot 10^{13}$</td>
</tr>
<tr>
<td>200</td>
<td>$3.6 \cdot 10^{13}$</td>
</tr>
<tr>
<td>250</td>
<td>$2.5 \cdot 10^{13}$</td>
</tr>
<tr>
<td>300</td>
<td>$2.5 \cdot 10^{13}$</td>
</tr>
<tr>
<td>120</td>
<td>$5.0 \cdot 10^{14}$</td>
</tr>
<tr>
<td>180</td>
<td>$4.5 \cdot 10^{14}$</td>
</tr>
<tr>
<td>130</td>
<td>$2.4 \cdot 10^{14}$</td>
</tr>
<tr>
<td>180</td>
<td>$2.4 \cdot 10^{14}$</td>
</tr>
<tr>
<td>230</td>
<td>$2.3 \cdot 10^{14}$</td>
</tr>
<tr>
<td>300</td>
<td>$2.1 \cdot 10^{14}$</td>
</tr>
<tr>
<td>380</td>
<td>$2.1 \cdot 10^{14}$</td>
</tr>
<tr>
<td>450</td>
<td>$2.0 \cdot 10^{14}$</td>
</tr>
</tbody>
</table>

Table 3.1: $N(E_F)$ for various annealing temperatures $T_i$ calculated from best fits of the data presented in Fig. 3.3. Calculated with Eq. 3.2 setting $\alpha^{-1} = 10 \text{ Å}$. 

4 Å Fe/130 Å ZnSe

18 Å Fe/150 Å ZnSe

60 Å ZnSe/12 Å Fe
Finally, the origin of the interface defect-states remains a subject of speculations. We may state that rough interfaces lead to a higher stability of the defect states which is also evidenced by magnetic measurements [28]. Further, the exchange of Fe by Co does not alter the transition temperature. This indicates that the transition is governed by the structural stability of the ZnSe.

In order to stimulate the discussion we would like to suggest two possibilities which could stabilize defects at Fe-ZnSe interfaces:

- The metal-semiconductor interface may be strained which might lead to defects. The measured density \( N(E_F) \approx 1 \times 10^{13} \text{eV}^{-1} \text{cm}^{-2} \) and an assumed level width of \( \Delta E_S \approx 0.1 \text{eV} \) yields an estimation of the absolute density of defects of \( N \approx 10^{12} \text{cm}^{-2} \). This means that there is a defect state every 100 Å. Strain takes several rows of atoms to be established and therefore this value supports the suggestion. Moreover, the annealing temperature can lead to small structural changes which in this case would be sufficient to annihilate the defects.

- Fe impurities in ZnSe are known to be Fe\(^{3+}\) ions replacing Zn\(^{2+}\) [29]. This impurity obviously can bind an electron. However, the energy level of Fe donors in ZnSe is deep lying, about 1.7 eV below \( E_G \) [30] which means that the extension of the donor orbital is small. This reduces the capacity of long range interaction which is necessary for the transmission of a magnetic exchange. If this donor is located close to an interface the nearby metal surface may influence the energy of the donor. One might think of a mirror charge established in the Fe layer which perturbs the donor and lifts its energy level. Co levels in ZnSe are even deeper lying (\( E_C - E_S = 2.2 \text{eV} \)) [31] which could be an explanation why in Co/ZnSe/Co trilayers heat-induced exchange has not been found [32,33].
Chapter 4

The Molecular-Orbital Model

4.1 Introduction

The knowledge of the importance of interface defect-states for the occurrence of heat-induced effective exchange coupling gives us the inspiration to devise a new model for the coupling. The concept of this model differs from any known description of magnetic coupling mechanisms in solid state physics. However, the magnetic interaction of this model is analogue to the spin interaction in chemical bindings. Therefore we call this concept “molecular-orbital model”.

First of all, we briefly recall the requirements for a model of heat-induced exchange coupling. The model should lead to antiferromagnetic coupling across an amorphous, semiconducting spacer layer in the spacer-thickness range of about 20 Å. At the upper edge of this range the size of the interaction should decrease and finally disappear. At the lower edge the coupling should exhibit a ferromagnetic interaction. However, the occurrence of ferromagnetic coupling for very thin spacers is not decisive as in this thickness range other effects may be involved. Further, the temperature dependence of the coupling should result to be positive with a saturation behavior at temperatures above 100 K. It must be considered that the coupling does not depend on the semiconductors energy gap, rather a dependence on the dielectric constant should appear.

Several earlier approaches have been made in order to model a coupling across semiconductors. So far, k-dependent tunneling [34], direct tunneling [35], resonant tunneling [13], tunneling across defect states [36], excitons in a direct band gap [37] and quantum size effects in a double quantum well [38] have been studied. The coupling strength mediated by k-dependent or direct tunneling exponentially depends on the size of the semiconductors energy gap. As well, a mediation by excitons in a direct band gap depends on the band gap. Therefore, these models do not apply. Resonant tunneling, however, is able to describe an interaction with a positive temperature behavior, even a saturation behavior results. Still, it remains unclear how an antiferromagnetic interaction within one range of spacer
Chapter 4. The Molecular-Orbital Model

thickness shall be explained. Size effects in a double quantum well can reproduce the thickness dependence of the coupling. However, the temperature coefficient results to be negative, moreover, the assumptions of the model do not fully coincide with the experimental situation. Finally, the work on tunneling across defect states claims to explain antiferromagnetic coupling with a spacer thickness dependence in agreement with the experiment. However, the line of arguments is unclear and the report does not treat the temperature dependence of the coupling.

Shallow interface defect-states which interfere across the spacer layer, on the other hand, do not depend on the size of the energy gap and therefore fulfill an important requirement so far. In the reminder of this chapter we sketch the concept of the "molecular-orbital model", we present an approximate calculation and we compare the calculated results with the experimental data.

4.2 The Coupling Mechanism

Let us consider an amorphous semiconductor layer of thickness $d$ embedded between two ferromagnetic metal layers of thickness much larger than $d$. The semiconducting material is characterized by a dielectric constant $\varepsilon$ and a reduced mass $m^*$. The defect states in the semiconductor bulk material are neglected at a first step. The ferromagnetic metal layers are characterized by a spin polarized free electron gas and a chemical potential $\mu$. At the interfaces localized electron states shall be present in the semiconducting material. We assume these electron states to be shallow donors and describe them as ground states of hydrogen-like impurity states. These states shall have large extensions due to the screening of the central charge by the dielectricity of the semiconductor. The extensions of these 1s-like electron states are so large that they may overlap across the spacer layer and in this way mediate the effective exchange coupling between the ferromagnets. The density of donor states at one interface $N$, however, shall be low enough so that the donors do not interact along the interfaces.

Metal-semiconductor junctions cause Schottky barriers related with depletion layers. The trilayer considered in this model is no exception, a possible charge transfer between the metal layers and the semiconductor gives rise to electrical dipoles across the interfaces. Since $d$ is small the effect of these dipoles can be approximated by a shift in energy between the band structures of the metal layers and the semiconductor.

The coupling mechanism is illustrated by the energy schemes depicted in Fig. 4.1. Two configurations with the magnetizations aligned parallel (FM) and antiparallel (AFM) are distinguished. On the two energy scales on each picture the relevant electron states at the two interfaces of the sample are shown. The horizontal scale not only includes spatial position but also density of states. "Up" and "down" spin states are placed to the right and to the left hand side of each energy scale, respectively. The spin polarized $d$-bands represent the relevant
4.2. The Coupling Mechanism

Figure 4.1: The molecular-orbital model. On the energy scales the states at the “left” and “right” interfaces of two ferromagnetic layers separated by a semiconducting spacer layer are shown. Parallel and antiparallel alignments of the magnetizations are distinguished in the upper and lower parts, respectively. The horizontal axis shows spatial position and density of states. The spin-split d-bands represent the ferromagnets, $s^*_{(\uparrow\downarrow)}$ are the donor states at the interfaces, and $\mu$ is the chemical potential. The levels between the energy scales are overlapping donor states forming molecular orbitals in the spacer. The energies of these molecular orbitals depend on the spin configuration which gives rise to the effective exchange coupling.

electron states of the ferromagnetic layers. The $s^*_{(\uparrow\downarrow)}$-states represent the shallow donor states. Levels of overlapping donor states are drawn in between the energy scales. $\mu$ finally is the chemical potential of the system.

The mechanism of the coupling involves two magnetic interactions, namely the coupling of the donor states to the nearby ferromagnets at the interface and the coupling among overlapping donor states across the semiconductor.
First, we consider the magnetic coupling of the donor states with the nearby ferromagnet at the corresponding interface. The donor orbitals overlap the ferromagnetic layer considerably and therefore we describe this coupling in mean-field approximation by a strong exchange field, the Weiss field $H_w$. The magnetic energy of an electron with magnetic moment $m$ in this field is given by $E_m = -m \cdot H_w$. In the ground state, $m$ is parallel to the field. A magnetic moment standing antiparallel to $H_w$ thus gains an energy of $2mH_w$ relative to the ground state. A Weiss field is approximately $H_w \sim 10^7$ Oe which yields $2mH_w$ to be of the order of 1 eV. At ambient temperatures this energy is huge compared to $kT$. Consequently, in Fig. 4.1 the $s^*$-states with antiparallel moment are drawn at a highly elevated energy. The magnetic moments of the donor states are therefore strongly coupled and aligned parallel to the magnetization of the nearby ferromagnet. This allows us, even at ambient temperatures, to consider the magnetic and the spin configurations to be always the same.

The exchange interaction between overlapping donor states is much weaker and therefore it is the decisive one. Because of the low density of donor states at each interface, we only have to consider the interaction across the spacer, i.e., of one pair of donor states situated at the two interfaces at opposite positions, let us say at the “right” and at the “left” interface. The Pauli principle requires that the molecular-orbital wave function with parallel spins has a lower probability amplitude within the spacer layer than the one with antiparallel spins. In Fig. 4.1 this consequence of quantum mechanics is symbolically represented with overlapping and separated circles for antiparallel and parallel spin configurations, respectively. This inequality causes an energy difference for interfering donors with different spin configurations which eventually drives the effective exchange coupling. In analogy with singlet and triplet states the level of antiparallel spin configuration is always lower than the one of parallel configuration. Therefore, if all interfering donor states are occupied an antiferromagnetic coupling is preferred.

However, if all interfering donor states are empty no coupling results. The temperature dependence of the effective coupling strength $J$ thus is a consequence of thermal repopulation of the donor states. In this thermodynamical picture the Fe layers are the particle reservoirs with chemical potential $\mu$.

Let us roughly and qualitatively estimate the results of this model. In a range of spacer thickness where the donor states interfere an energy difference is caused and antiferromagnetic coupling prevails. At spacer thicknesses larger than the extension of the donor states there is no interference and therefore no coupling should be found. If $\mu$ is lower than the level of the donor states, as depicted in Fig. 4.1, there are no interfering donor states at 0 K and no coupling should result. With rising temperature these states get occupied and the coupling strength increases. At some temperature, depending on the relative position of $\mu$ and the donor states, a maximum share of donor states is occupied and the coupling strength saturates.
4.3 An Approximate Calculation

The mathematical description of the “molecular-orbital model” is developed in two steps. First, we calculate the relative energies of the electron states which are relevant for the coupling mechanism. We separately consider the two configurations with the magnetizations aligned parallel and antiparallel. Second, we calculate the occupation of these levels for the two configurations. Subtracting the resulting energies of the two configurations we eventually acquire an equation for the effective coupling strength $J$.

The relevant energies for the coupling are the donor levels and the chemical potential $\mu$. The unperturbed donor levels $E_d$ do not depend on the spin configuration while the levels of interfering donors $E_{\uparrow\downarrow}$ and $E_{\downarrow\uparrow}$ are determined by the configuration of their spins.

In order to calculate the energy levels of the shallow donors we neglect the Weiss fields and the nearby metallic surfaces and treat the donors as hydrogen-like atoms with two corrections, namely the screening factor $\varepsilon$ and the reduced mass $m^*$. The standard Hamiltonian for shallow donors reads [39]

$$H_S = \frac{\hbar^2}{2m^*} \nabla^2 - \frac{\varepsilon^2}{\varepsilon r}$$  \hspace{1cm} (4.1)

of which the ground state is a 1s-like orbital

$$\phi(\varepsilon, m^*) \sim \left( \frac{m^*}{m \varepsilon a_0} \right)^{3/2} \exp \left\{ - \frac{m^* r}{m \varepsilon a_0} \right\}$$  \hspace{1cm} (4.2)

where $a_0 = 0.52$ Å is the Bohr radius. The corresponding energy is

$$E_S = \frac{m^*}{m \varepsilon^2} E_0$$  \hspace{1cm} (4.3)

where $E_0 = -13.6$ eV is the Rydberg energy.

A modified Bohr radius $a_S$ may be defined as $a_S = a_0 \cdot \varepsilon \cdot m/m^*$. The introduction of a screening factor $\varepsilon > 1$ and a reduced mass $m^* < m$ obviously enlarges the spatial extension of the impurity states, as required. We note that the variation of both parameters qualitatively has the same effect. Therefore, for the sake of simplicity, we choose $m^* = m$ and only retain $\varepsilon$ as a free parameter. Because of their large spatial extensions the donor orbitals from the “left” and the “right” interface, indeed, may overlap across the semiconductor to form giant molecular orbitals.

For the calculation of the interfering levels we consider a pair of shallow donors situated at opposite positions at the “left” (L) and the “right” (R) interface. In order to develop Hamiltonian and wave functions the ferromagnetic layers are neglected at a first step. This allows us to follow the molecular-orbital method [40].

The Hamiltonian consists of Coulomb interactions only, i. e., of the single electron energies $H_{S,L}$ and $H_{S,R}$, where L and R denote “left” and “right”, and
of the Coulomb interactions across the spacer layer. The electrons are labeled 1 and 2, and $r_{j,i}$ stands for the distance $|r_j - r_i|$ with $j = R, L$ and $i = 1, 2$.

$$H = H_{S,L} + H_{S,R} + \frac{e^2}{\varepsilon} \left(-\frac{1}{r_{L,2}} - \frac{1}{r_{R,1}} + \frac{1}{r_{1,2}} + \frac{1}{d}\right)$$

(4.4)

For the wave functions the orbitals $\phi_L(r)$ and $\phi_R(r)$ are combined to bonding and antibonding molecular-orbitals, respectively:

$$\psi_{+,\sigma}(r, s) \sim [\phi_L + \phi_R](r)\chi_\sigma(s)$$

(4.5)

$$\psi_{-,\sigma}(r, s) \sim [\phi_L - \phi_R](r)\chi_\sigma(s)$$

(4.6)

$\chi_\sigma(s)$ denotes the spin wave-function with $\sigma = \uparrow, \downarrow$ and $s$ is the $z$-component of the spin with the values $\uparrow, \downarrow$. The value of the spin wave-functions is $\chi_\uparrow(\uparrow) = 1$, $\chi_\downarrow(\downarrow) = 1$ and zero otherwise. In order to populate the molecular orbitals by two electrons the Pauli principle must be taken into account. Therefore, the wave functions are combined by a Slater determinant. In the following $1, 2$ stand for $r_1, r_2$ and $s_1, s_2$ for orbital wave-functions and spin wave-functions, respectively.

$$\Psi_{++}(1, 2) \sim \psi_{+,\sigma}(1)\psi_{+,\sigma'}(2) - \psi_{+,\sigma}(2)\psi_{+,\sigma'}(1)$$

(4.7)

$$\Psi_{+-}(1, 2) \sim \psi_{+,\sigma}(1)\psi_{-,\sigma'}(2) - \psi_{+,\sigma}(2)\psi_{-,\sigma'}(1)$$

(4.8)

After neglecting the smallest terms containing $\phi_L(1)\phi_L(2)$ and $\phi_R(1)\phi_R(2)$ from Eqs. 4.7 and 4.8 the well known singlet and triplet states $\Psi_{\text{sing}}$ and $\Psi_{\text{trip}}$ result:

$$\Psi_{\text{sing}}(1, 2) \sim [\phi_L(1)\phi_R(2) + \phi_L(2)\phi_R(1)][\chi_\sigma(1)\chi_\sigma'(2) - \chi_\sigma(2)\chi_\sigma'(1)]$$

(4.9)

$$\Psi_{\text{trip}}(1, 2) \sim [\phi_L(1)\phi_R(2) - \phi_L(2)\phi_R(1)][\chi_\sigma(1)\chi_\sigma'(2) + \chi_\sigma(2)\chi_\sigma'(1)]$$

(4.10)

$\sigma, \sigma'$ are identified by all permutations of $\uparrow$ and $\downarrow$. This permutation leads to one spin state for $\Psi_{\text{sing}}$ and three spin states for $\Psi_{\text{trip}}$ [41].

These wave functions are heavily perturbed if each of the donors interacts with the magnetization of a nearby ferromagnet. Close to the interfaces the electrons experience the Weiss fields. Their energy is lowered by the magnetic energy $E_m = mH_w$ if their magnetic moment $m$ is aligned parallel to the respective Weiss field. Outside the ferromagnetic layer $H_w$ decreases rapidly such that the electrons have an elevated amplitude towards the respective interface. Particularly in case of antiparallel alignment of the magnetizations, the symmetry of the molecular orbitals is broken.

In order to take this perturbation into account we introduce two parameters $\alpha$ and $\beta$ into the molecular orbitals. Because of the broken symmetry we have to consider two linear combinations of the bonding and antibonding orbitals:
4.3. An Approximate Calculation

\[ \psi_{L, \sigma}(r, s) = [\alpha \phi_L + \beta \phi_R](r) \chi_{\sigma}(s) \]  
\[ \psi_{R, \sigma}(r, s) = [\beta \phi_L + \alpha \phi_R](r) \chi_{\sigma}(s) \]

The parameters \( \alpha \) and \( \beta \) would have to be optimized now. For the sake of simplicity and for a very first approximation we set \( \alpha = 1 \) and \( \beta = 0 \). \( \psi_{L, \sigma}(r, s) \) and \( \psi_{R, \sigma}(r, s) \) combined in a Slater determinant lead to the wave functions for antiparallel and parallel alignment, \( \Psi_{\uparrow \downarrow} \) and \( \Psi_{\uparrow \uparrow} \), respectively. Note that there exists only one wave function for each magnetic alignment.

\[ \Psi_{\uparrow \downarrow}(1, 2) = \frac{1}{\sqrt{2}} \left[ \phi_L(1) \chi_{\uparrow}(1) \phi_R(2) \chi_{\downarrow}(2) - \phi_L(2) \chi_{\uparrow}(2) \phi_R(1) \chi_{\downarrow}(1) \right] \]
\[ \Psi_{\uparrow \uparrow}(1, 2) = \frac{1}{\sqrt{2(1 - S^2)}} \chi_{\uparrow}(1) \chi_{\uparrow}(2) [\phi_L(1) \phi_R(2) - \phi_L(2) \phi_R(1)] \]

where \( S \) is the overlap integral \( \int \phi_L(r) \phi_R(r) d^3r \). The derived wave functions (Eqs. 4.13 and 4.14) and the Hamiltonian (Eq. 4.4) allow to calculate the energies for antiparallel and parallel alignment \( E_{\uparrow \downarrow} \) and \( E_{\uparrow \uparrow} \)

\[ E_{\uparrow \downarrow} = E_S(\varepsilon) + \frac{1}{2} \left[ \frac{e^2}{\varepsilon \tilde{d}} + V_c(d, \varepsilon) \right] \]
\[ E_{\uparrow \uparrow} = E_S(\varepsilon) + \frac{1}{2} \left[ \frac{e^2}{\varepsilon \tilde{d}} + \frac{V_c(d, \varepsilon) - V_{ex}(d, \varepsilon)}{1 - S^2(d, \varepsilon)} \right] \]

\( V_c \) and \( V_{ex} \) are the Coulomb and exchange energies, respectively.

\[ V_c = \int \int \phi_L^2(r_1) \phi_R^2(r_2) \frac{e^2}{\varepsilon} \left( -\frac{1}{r_{L,2}} - \frac{1}{r_{R,1}} + \frac{1}{r_{1,2}} \right) d^3r_1 d^3r_2 \]
\[ V_{ex} = \int \int \phi_L(r_1) \phi_R(r_2) \frac{e^2}{\varepsilon} \left( -\frac{1}{r_{L,2}} - \frac{1}{r_{R,1}} + \frac{1}{r_{1,2}} \right) \phi_L(r_2) \phi_R(r_1) d^3r_1 d^3r_2 \]

The orbitals \( \phi_{L(R)} \) are inserted from Eq. 4.2. We resolve \( V_c \) and \( V_{ex} \) using the integrals by Sugiura [42] and then numerically evaluate \( E_{\uparrow \downarrow} \) and \( E_{\uparrow \uparrow} \) with the free parameter \( \varepsilon = 10 \), which roughly corresponds to the value of ZnSe. The results are compiled in Fig. 4.2.

The relative position of the chemical potential \( \mu \) is not easy to determine. As mentioned, a charge transfer at the metal-semiconductor junction may result in a shift of the respective energy structures. The dependence of this shift on the electronic structures of the materials, additional influences of metal-induced gap states, interface and bulk defect-states is still a subject of discussion [43]. Therefore, we use \( E_S - \mu \) as the second free parameter of the model, represented in Fig. 4.2 as a broken line at a physical meaningful position.
Chapter 4. The Molecular-Orbital Model

Figure 4.2: Calculated energy levels versus distance between the interfering donors for antiparallel (left panel) and parallel (right panel) spin configurations, respectively. The free parameter $\varepsilon$ is chosen to be 10, which roughly corresponds to the dielectric constant of ZnSe ($\varepsilon_{\text{ZnSe}} = 9.2$). $E_{\uparrow\uparrow}$ are the energies of interfering electrons, $E_S$ is the energy of a noninteracting donor state, set to zero, and $\mu$ is the chemical potential. $E_S - \mu$ is treated as a free parameter.

The compiled energies in Fig. 4.2 already indicate the behavior of $J$. As $E_{\uparrow\uparrow}$ is always lower than $E_{\uparrow\downarrow}$ antiferromagnetic coupling is expected to predominate. $E_{\uparrow\uparrow}$ has a characteristic minimum which for $\varepsilon = 10$ occurs at about 10 Å. In this range the donors are most likely occupied and if the minimum is lower than $\mu$, as suggested in Fig. 4.2, antiferromagnetic coupling occurs already at 0 K. A variation of $\varepsilon$ to smaller and bigger values shifts the energy minimum to shorter and larger distances, respectively. The value of the energy minimum relative to $E_S$ is not accurate as the levels of interfering donors are calculated in rough approximation. For the Slater determinant, we use orbitals $\phi$ of which the amplitude is centered only at the position of one donor; i.e., we set the parameters $\alpha = 1$ and $\beta = 0$. However, if we apply valence-bond theory, which combines orbitals with finite amplitude at both donor positions ($\alpha = \beta$), the contribution of the exchange energy is larger and the energy minimum for $E_{\uparrow\uparrow}$ results to be much deeper. The two mentioned wave functions are expected to approximate the precise molecular-orbital wave function from two extremal points. Therefore, we expect the energy minimum in an improved approximation with optimized parameters $\alpha$ and $\beta$ to be lower than the one in the present case.

The coupling strength $J$ depends on the population of the energy levels. In order to maintain overall charge neutrality we must allow for transfer of electrons from or to the metal layers, which serve as particle reservoirs. We therefore have to consider the thermodynamic potential $\Omega = \sum_i n_i \varepsilon_i - \mu \sum_i n_i$, where $E_i$ are the one particle energies $E_S$, $E_{\uparrow\downarrow}$ and $E_{\uparrow\uparrow}$ and $n_i$ their respective occupations. The
4.3. An Approximate Calculation

effective coupling strength $J$, which phenomenologically is defined in Eq. 1.1, is identified with the difference of the thermodynamic potentials per unit area $A$ [6].

$$J = \frac{1}{A} (\Omega_{\uparrow\downarrow} - \Omega_{\uparrow\uparrow})$$

(4.19)

$\Omega_{\uparrow\downarrow}$ and $\Omega_{\uparrow\uparrow}$ are the thermodynamic potentials for the respective spin configurations.

The occupations $n_i$, on one hand, are governed by the Fermi distribution $f(E_i) = (1 + \exp \{(E_i - \mu)/kT\})^{-1}$ since the interfering electrons still are fermions. On the other hand, $n_i$ strongly depend on the density of donor states at one interface $N$. Basically, the occupation may be considered as the available states of a specific energy level $N^*(E_i)$ weighted by the Fermi distribution, $n_i = N^*(E_i)f(E_i)$. However, $N^*(E_i)$ can not simply be identified with $2N$, the density of donor states at the two interfaces. The reason is that electrons may have different energies on the very same donor state. On one hand, the electron energy in a pair of potentially interfering donor states amounts to $E_S$ for single occupation. On the other hand it equals $E_{\uparrow\downarrow}$ or $E_{\uparrow\uparrow}$ for double occupation, depending on the spin configuration. In order to properly account for this we first make all donor states at both interfaces available and calculate the share of doubly occupied donor pairs.

$$n_{\uparrow\downarrow(\uparrow\uparrow)} = 2Nf(E_{\uparrow\downarrow(\uparrow\uparrow)})$$

(4.20)

In a second step the remaining empty donor states are made available for single occupation. As single occupation means that only one state of a pair is populated, hence $N^*$ contains $N$ once and further a prefactor which withdraws the states which have been doubly occupied.

$$n_S = \left[1 - f(E_{\uparrow\downarrow(\uparrow\uparrow)})\right]Nf(E_S)$$

(4.21)

$N$ is treated as the third free parameter of the model.

With the knowledge of the occupations we may write the thermodynamical potentials $\Omega_{\uparrow\downarrow}$ and $\Omega_{\uparrow\uparrow}$.

$$\Omega_{\uparrow\downarrow(\uparrow\uparrow)} = AN\{2f(E_{\uparrow\downarrow(\uparrow\uparrow)}))[E_{\uparrow\downarrow(\uparrow\uparrow)} - \mu] + [1 - f(E_{\uparrow\downarrow(\uparrow\uparrow)})]f(E_S)[E_S - \mu]\}$$

(4.22)

Introducing $\Omega_{\uparrow\downarrow}$ and $\Omega_{\uparrow\uparrow}$ into Eq. 4.19 we finally get an equation for the coupling strength $J$.

$$J = N\{2f(E_{\uparrow\downarrow})[E_{\uparrow\downarrow} - \mu] - 2f(E_{\uparrow\uparrow})[E_{\uparrow\uparrow} - \mu] + [f(E_{\uparrow\uparrow}) - f(E_{\uparrow\downarrow})]f(E_S)[E_S - \mu]\}$$

(4.23)

We present numerical results of $J$ in Fig. 4.3 for one appropriate choice of the free parameters. The screening factor $\varepsilon = 10$ lies in the range of the dielectric
constant of ZnSe ($\varepsilon_{ZnSe} = 9.2$), the density of defect states $N = 1 \times 10^{12}$cm$^{-2}$ is realistic for this type of interfaces and it is supported by the transport measurements on Fe/ZnSe heterostructures (see end of chapter 3). The relative position
of $\mu$ is freely chosen to be $E_s - \mu = 2$ meV such that it corresponds to a characteristic temperature in the range of about 50 K. In Fig. 4.3 the dependences on the spacer thickness (top panel) as well as the temperature behaviors (bottom panel) are compiled.

4.4 Discussion

The numerical results presented in Fig. 4.3 agree amazingly well with the experimental data shown in Fig. 2.2 and Fig. 2.3. With a physically meaningful choice of the three free parameters, even in a roughly approximated calculation, we find the requirements for the model perfectly fulfilled. First of all, the antiferromagnetic coupling occurs in a spacer-thickness range of about 10 Å which well corresponds to the experimental observations. At low temperatures this range is quite narrow and it broadens towards larger spacer thicknesses with rising temperature. For thick spacers we find weak or no coupling. At the lower edge of the antiferromagnetic thickness range ferromagnetic coupling is found. It does not completely predominate, at variance with the experimental observations. However, very thin spacers can not be expected to perfectly separate the ferromagnetic layers from each other. Therefore, pinholes may occur and align the magnetizations parallel. Eventually, it is hard to resist emphasizing the detail that even the heat-induced sign change, measured at the thicker edge of the antiferromagnetic range, is reproduced by the model for $d \approx 16$ Å. The calculated temperature dependences exhibit a positive temperature coefficient, which is the key feature of exchange coupling across amorphous semiconductors. In particular, one finds good agreement to the experimental data for larger spacer thicknesses; the coupling strength saturates above 100 K. Finally, the magnitude of the coupling strength is well reproduced, the calculated and experimental results turn out to be within the same order of magnitude: $J$ amounts to $10^{-6}$ J m$^{-2}$ at thermal saturation.

The quality of a model is indicated by the agreement of its results with the experimental data. However, the quality augments considerably if, upon a variation of the free parameters, the results of such a model behave in a physically reasonable way. In the present case, the easiest parameter to understand is the number of donors per interface area $N$. The coupling strength $J$ is proportional to $N$, and thus a variation of $N$ does not result in a qualitative change of $J$. As the chosen value of $N$ is based on transport measurements, the reliability of the calculated magnitude of $J$ is supported. The screening factor $\varepsilon$ and the position of the chemical potential $\mu$, in contrast, influence the thickness and temperature dependences of $J$. However, we wish to emphasize that the gross features of $J$ persist upon a considerable variation of the free parameters, as is shown in Fig. 4.4. On one hand an increasing $\varepsilon$ shifts the thickness range where the coupling occurs to larger spacer thicknesses and it reduces the coupling strength slightly; compare Fig. 4.4, panels a) and b). On the other hand the position of $\mu$
Chapter 4. The Molecular-Orbital Model

Figure 4.4: Calculated effective coupling strength $J$ vs spacer thickness $d$ (left panels), and vs temperature $T$ (right panels) under variation of the free parameters $\varepsilon$ and $E_S - \mu$. a) $\varepsilon = 7, E_S - \mu = 2 \text{ meV}$. b) $\varepsilon = 15, E_S - \mu = 2 \text{ meV}$. c) $\varepsilon = 10, E_S - \mu = 0 \text{ meV}$. d) $\varepsilon = 10, E_S - \mu = 4 \text{ meV}$. The density of defect states $N = 1 \times 10^{12} \text{ cm}^{-2}$ is held constant for all calculations.
4.5 Further Investigations

mainly influences the temperature dependence of $J$. The larger the energy gap $E_S - \mu$ the higher the temperature where $J$ saturates, compare Fig. 4.4, panels c) and d).

In conclusion we propose a molecular-orbital model of heat induced exchange coupling between ferromagnetic layers separated by an amorphous-semiconductor spacer layer. The mechanism is based on the assumption of localized, weakly bound electron states to exist at the semiconductor-metal interfaces. They are described as ground states of hydrogen-like donor states which are screened by the dielectricity of the semiconductor. They can form molecular orbitals across the spacer layer and thus mediate an exchange interaction. The present calculation, even with rough approximations, yields amazingly good agreement with the experimental data. Moreover, the calculated results behave reasonably upon the variation of the free parameters. Hence, we are confident that the molecular-orbital model will persuade as a valuable description of heat-induced effective exchange coupling.

4.5 Further Investigations

The molecular-orbital model presented in this thesis is a new concept of a magnetic coupling, however, it is calculated in the roughest approximation. Therefore, it is expected to stimulate further theoretical activity.

The most interesting task is the precise description of the interfering donor wave functions, the "molecular orbitals". As we stated in section 4.3 we work in a very first approximation which calls for improvement. An optimization of the parameters $\alpha$ and $\beta$ or even a new description would lead to a better calculation of the exchange energies. On the same footing the description of the single donor states should be improved. The influence of the nearby metal layer has to be considered which will perturb the geometry and the energy of the donor states. It is to be expected that the donor levels do not form singular distributions. A finite width of the energy distribution will mainly correct the coupling behavior at low temperatures.

This theoretical work needs to be supported by experimental evidence on the origin of the donor states. For example, this origin could be unveiled by an artificial implantation of impurities which are known to form shallow donors. In order to get these impurities close to the interfaces, as requested by the model, one would have to evaporate the multilayer like a good Italian lasagne. A submonolayer of the impurities has to be evaporated between the ferromagnetic and the semiconductor layer like cheese crumbs sprinkled between the pasta sheets and the tomato sauce. This sample may be expected to be stable at room temperature and it could be examined by photoemission for example. This experiment is also of technical interest because the stability at room temperature is a necessity for an application of heat-induced exchange coupling in technical devices.
Chapter 4. The Molecular-Orbital Model

As mentioned in the beginning of this thesis, the molecular-orbital model closes a circle which starts a new challenge. The insight that the population of interface donor states, which in the present case is governed by thermal excitation, causes magnetic coupling leads to the question if this population also could be influenced by an applied voltage. A *voltage-controlled exchange coupling*, eventually, would definitely lead to powerful technical applications.
Chapter 5

On the Way to Voltage-Controlled Exchange Coupling

5.1 Motivation

The discovery of the Giant Magneto Resistance (GMR) [17,18] has moved the concept of Magnetic Random Access Memory (MRAM) into the spotlight of interest [44–48]. MRAM consists of ferromagnetic multilayers which store binary digits by parallel or antiparallel magnetic alignment. The electronic resistivity in ferromagnetic multilayers is sensitive to magnetic alignment which allows to "read" the digits by applying a voltage to the multilayer. In order to realize MRAM also a "writing" process is needed. This means that a magnetic alignment must be influenced by applying a voltage. Slonczewski suggested to drag a current perpendicular to a multilayer consisting of two ferromagnetic layers separated by an insulating tunnel barrier [49]. He also suggested to drag this current across a point contact in order to achieve high current densities [50]. Recent experiments revealed a current-induced excitation of ferromagnetic layers [51] and finally a current-induced switching of the magnetic alignment in ferromagnetic multilayers [19,52].

However, giant current densities in the range of $10^9$Acm$^{-2}$ are required to make the magnetic switching to occur. This is the main cause why MRAM still is not realized. Therefore, an effect which could influence the magnetic alignment by applying a voltage onto a multilayer accompanied by only weak or no current would revolutionize storage devices.

The molecular-orbital model nourishes the conjecture that a voltage applied perpendicularly to a magnetic trilayer could influence the exchange coupling or even switch the magnetic configuration. Heat-induced exchange coupling is caused by overlapping donor states which are populated by thermal excitations.
If an applied voltage controls this population it also could control the exchange coupling. This would be a big step on the way to a non-dissipative “writing” process. If for example at high temperatures the donor states are emptied by the voltage the antiferromagnetic coupling would disappear. The alignment of the magnetizations could be switched by a small external field without any energy dissipation.

5.2 Experimental Concept

The challenge of measuring a voltage-controlled exchange coupling is the application of a voltage perpendicular across the layers. As we choose a sample which exhibits the heat-induced coupling phenomenon the thickness of the semiconductor spacer layer is set to about 20 Å. At these thicknesses pinholes are very likely even if the substrate is very flat. Furthermore, the metal layers must be contacted without destroying the spacer layer. In order to solve these problems we suggest a sample layout as depicted in Fig. 5.1.

We use an insulating substrate (SiO$_2$) with a polished surface. Au gates are evaporated onto this surface, one to the left and five to the right. They all are contacted to separate electrodes fixed on the sample holder. With a mask the ground layer, the magnetic driver, consisting of 90 Å Co and 6 Å Fe is evaporated

Figure 5.1: Layout of the sample proposed [28] for measurements of voltage-controlled exchange coupling. The thickness of the ZnSe layer is kept at 23 Å. The area of the overlapping Fe layers (arrow) is chosen to be 0.2 mm$^2$ in order to minimize the possibility of short circuits across the ZnSe spacer. Five areas form separate trilayers.
5.2. Experimental Concept

on top of the left gate. A ZnSe layer of 23 Å covers the bottom Fe/Co layer and separates it from the top Fe layer. The top Fe layer then is evaporated in stripes of 0.5 mm width on top of the right Au gates overlapping the magnetic driver by about 0.4 mm. The areas of the overlapping ferromagnetic layers is kept small in order to inhibit the possibility of pinholes across the spacer. Furthermore, the number of five similar but separated “samples” augments the statistical possibility for a short-circuit-free trilayer.

For the method of the measurement we propose Spin-Polarized Scanning Electron Microscopy (Spin-SEM). This method allows us to image the polarization of a very small sample surface and it also gives us information on the behavior of possible magnetic domains and on the growth of the layers. With an unpolarized, focussed electron beam the sample surface is scanned. The polarization of the emitted secondary electrons is analyzed in a Mott detector. For the coupling measurement we proceed the same way as in chapter 2 measuring the sign of the coupling by SPSEE. The magnetization of the magnetic driver must be hard and uniaxial such that the measurement on the top Fe layer yields the sign of the coupling. Moreover, if the hysteresis loop of the top Fe layer is linear, see Fig. 5.2, also a change of the compensation field $H_{\text{comp}}$ and hence of the coupling strength $J$ can be detected by the measurement of the surface polarization at remanence.

The best growth conditions for a sample with coupling properties prevail in our own vacuum chamber. However, there is no Spin-SEM available. In order to produce the sample in our chamber and transfer it to the chamber of the IBM research laboratory Rüschlikon, where a Spin SEM is available, a special sample holder has been developed, see Fig. 5.3. This sample holder includes a male part of a plug with the electrodes contacted to the Au gates. For the evaporation the masks can be placed onto this sample holder. For the application of the voltage a contact ring, the female part of the plug, is put upon the bottom ring. The contacts are specially designed such that this plug works in UHV where the contact ring is brought upon the ground ring with a wobble stick.

![Figure 5.2: Schematic linear response $M(H)$ of a top ferromagnetic layer coupled by the coupling strength $J$ to a magnetic driver. Such a magnetic behavior allows to indirectly measure $J$ by the polarization $P$ of the sample surface at remanence. $M_s$ is the saturation magnetization, $M_R$ is the magnetization at remanence and $H_{\text{comp}}$ the compensation field, and $P \sim J$ for $M_R < M_s$.](image-url)
Chapter 5. On the Way to Voltage-Controlled Exchange Coupling

Figure 5.3: Sample holder for the measurements of voltage-controlled exchange coupling. A) Cu-basis, compatible to manipulator, B) macor ground ring, C) macor contact ring. Ground ring and contact ring are a plug which allows to contact the Au gates on the sample in vacuum. a) sample position, b) slit for fixing the contacting steel sheet, c) groove, position of steel sheet, d) thread for contacting screw, e) guiding pin, f) tube for the guiding pin. Au wires contact the Au gates on the sample with the steel sheets. By means of a wobble stick the contact ring is brought onto the ground ring where the screws contact the metal sheets. The screws finally are wired to feedthroughs. Picture by Ch. Muheim.
5.3 Results of Precursory Experiments

In order to produce a multilayer according to the requirements we first face the challenge to evaporate a magnetic driver onto a SiO₂ substrate with a non-crystalline surface. We choose Co as the main material because it has a much larger coercivity than Fe. We measure $H_c(\text{Co}) \sim 40$ Oe and $H_c(\text{Fe}) \sim 2$ Oe at room temperature. We find that we are not able to influence the anisotropy of a Co layer by an external field. However, if a thin Fe layer of about 10 Å thickness is evaporated onto the substrate first with an applied bias field of 60 Oe the adjacent Co layer gets an easy axis parallel to the bias field. We think that the magnetization of the Fe layer may be saturated by the bias field because of its small coercivity. The polarized Fe layer “triggers” the adjacent Co layer because the evaporated atoms experience the Weiss field of the ferromagnetic layer at the sample surface.

The heat-induced exchange coupling can only be measured if the Co surface is briefly sputtered with Ar at 2 kV before the next layers complete the sample. We interpret that the growth of the metal layer yields a rough surface and the sputtering may smooth it out. The sample is completed by 5 Å Fe, 23 Å ZnSe (both layers evaporated at room temperature) and 12 Å Fe (evaporated at 30 K). The spacer thicknesses $d_{\text{ZnSe}} \sim 23$ Å is chosen because for this spacer thickness the heat-induced behavior is strongest. The temperature dependence for this particular spacer thickness measured by the polarization at remanence is depicted in Fig. 5.4.

The data given in Fig. 5.4 testify that a sample completed by ZnSe and an Fe top layer meets the requirements for the forthcoming experiments. First of all, the behavior of the $M(H)$-responses of the sample surface is linear within the range of ±15 Oe. As examples the measurements at 150 K and 280 K are given on insets. The linear behavior allows us to measure the coupling strength indirectly by the surface polarization at remanence. The data given in the main panel, polarization versus temperature, reveal a heat-induced behavior – the coupling strength increases reversibly upon heating at temperatures below 150 K. In contrast to the measurements on a crystalline Cu substrate, presented in chapter 2, the antiferromagnetic coupling does not disappear upon annealing at room temperature, however, the properties of the top layers magnetization change. Supposedly the linear range of the $M(H)$-response gets narrower such that the compensation field exceeds this range at temperatures above 50 K. For the temperature dependence, the molecular-orbital model predicts a saturation behavior at higher temperatures. The decreasing absolute polarization above 200 K does not contradict the model. It is caused by a decreasing saturation magnetization which is demonstrated by the $M(H)$-responses. The data show that a measurement of the coupling strength monitored by the surface polarization is feasible. However, in the present case it would be restricted to compensation fields $H_{\text{comp}} < 15$ Oe and to temperatures $T < 200$ K.
Chapter 5. On the Way to Voltage-Controlled Exchange Coupling

Figure 5.4: Polarization at remanence vs temperature measured on the multilayer 12 Å Fe/23 Å ZnSe/Fe/Co/SiO$_2$. The insets depict $M(H)$-responses of the top layer ($P \sim M$) measured at 150 K and 280 K. As these responses are linear within a range of a few Oe the coupling strength may be measured indirectly detecting the surface polarization, compare also Fig. 5.2. In this case the measurement is limited to $H_{\text{comp}} < 15$ Oe and to $T < 200$ K as the saturation magnetization of the top layer decreases for higher temperatures.

In conclusion so far we state that the measurement of voltage-controlled exchange coupling is well prepared. Next steps to be taken are to build the sample holder and to evaporate the multilayers on it. We expect exciting measurements — which will rise more questions than giving answers.
Bibliography


Bibliography

Bibliography


Dank


Silvia Lüscher und Stefan Fischer waren einfach als wichtige Freunde da. Kaffee und Tratsch sind das Öl in der Maschinerie der Wissenschaft.

Curriculum Vitae

April 14th, 1970  Born in Richterswil ZH, citizen of Kirchleerau AG (Switzerland)

1977–1986  Rudolf Steiner-School Zürcher Oberland

1987–1991  Kantonsschule Pfäffikon SZ, Matura Typus C


1992–1997  Student at the Swiss Federal Institute for Technology (ETH Zurich), faculty of chemistry, domain of interdisciplinary sciences.

1993–1994  Collaboration with Prof. Dr. Ernst A. Brugger, FUNDES Switzerland. Several contributions within the topic of eco-efficiency.

1997  Diploma thesis “Growth and Magnetic Anisotropy of Ultra Thin Co-Films on Cu” at the IBM Research Laboratory Rüschlikon with PD Dr. Rolf Allenspach.

March 1997  Graduation from ETH Zurich. Degree: Dipl. Natw. ETH.

1997  Elaboration of a business plan to promote an entrepreneurs’ centre of FUNDES Argentina in Buenos Aires.

1997–2000  Teaching assistant and PhD student at the Laboratory for Solid State Physics at ETH Zurich in the group of Prof. Dr. Hans-Christoph Siegmann and Prof. Dr. Martin Landolt.

Zurich, June 13th, 2000
Lebenslauf

14. April 1970 Geboren in Richterswil ZII, Bürger von Kirchleerau AG

1977–1986 Rudolf Steiner-Schule Zürcher Oberland

1987–1991 Kantonsschule Pfäffikon SZ, Matura Typus C


März 1997 Abschluss des Studiums an der ETH Zürich. Titel: Dipl. Natw. ETH.

1997 Erarbeitung eines Businessplans für die FUNDES Stiftung Argentiniens in Buenos Aires.

1997–2000 Assistent und wissenschaftlicher Mitarbeiter am Laboratorium für Festkörperphysik der ETH Zürich unter Prof. Dr. Hans-Christoph Siegmann und Prof. Dr. Martin Landolt.

Zürich, den 13. Juni 2000