Novel materials for magnetic tunnel junctions

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vorgelegt von

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Chapter 1

Introduction

Conventional electronics is based on the charge of the electron to drive and manipulate electron currents. Recently, physical effects have been discovered that allow the control of electron motion using its spin. What began with the discovery of giant magnetoresistance (GMR) in the late 80s developed into a research field taunted “Spintronics” which has by now captivated the focus of many research groups around the globe.

A few years after the discovery of GMR, a much higher magnetoresistance effect was demonstrated in magnetic tunneling junctions (MTJs). MTJs consist of two ferromagnetic layers separated by a thin insulating layer. The thickness of this barrier is on the order of nanometers making the junctions true vertical nanostructures. Due to the small vertical dimensions the fabrication of MTJs relies on sophisticated deposition techniques in ultra high vacuum. In MTJs a current can flow between the electrodes upon application of a voltage bias due to quantum mechanical tunneling through the barrier. The resistance of the structure depends on the relative orientation of the magnetizations of the ferromagnetic electrodes. Many applications have been proposed for MTJs, e.g. read heads for hard disk drives or magnetic random access memory (MRAM). While MTJ read heads are commercially available at the moment there is intense developmental effort in the industry towards the creation of MTJ MRAMs which promise fast access times and high information density combined with non-volatility.

The focus of the research effort described in this thesis was to deepen the un-
derstanding of spin polarized tunneling in MTJs. Therefore the dependence of spin polarization on composition of certain rare earth–transition metal alloys was investigated highlighting the importance of tunneling matrix elements for the description of the tunneling process. Rare earth–transition metal alloys display a range of useful properties which will be outlined throughout chapter 3. Furthermore, the spin polarization of Fe and Co–Fe was measured using MgO barriers. Theoretical calculations predict high magnetoresistance values for fully epitaxial Fe/MgO/Fe MTJs. These predictions could partly be verified experimentally (chapter 4) paving the way for a comparison between theory and experiment that had not been possible to this extent before.

Given the fact that the experimental work for this thesis was done in an industrial research lab the implications of the research for actual device applications will be stressed throughout this thesis.
Chapter 2

Theoretical background and experimental techniques

2.1 Magnetic Tunnel Junctions

Magnetic tunnel junctions consist of two ferromagnetic metals (FM) separated by a thin (~20Å) insulating barrier (I). Application of a voltage bias at the electrodes leads to a tunneling current whose magnitude depends on the relative orientation of the magnetizations of the ferromagnetic layers. For conventional ferromagnetic metals (e.g. Co, Fe, and Ni) the resistance is higher when the magnetizations of the two electrodes are antiparallel as compared to parallel alignment.

The first successful tunnel junction was prepared by Julliere in the early 70s [1]. He used Co and Fe as electrode materials and Ge which was oxidized after deposition as the insulating barrier. A resistance change as high as 14% was observed at low temperatures and very low bias. After the initial discovery MTJs using other tunnel barriers (e.g. NiO [2] and Gd$_2$O$_3$ [3]) were explored but only small effects (<7% at 4.2 K) were observed. In 1995 two different groups (Miyazaki [4] and Moodera [5]) prepared MTJs using amorphous Al$_2$O$_3$ barriers and achieved TMR values much higher than previously reported (18% at room temperature and 30% at 4.2 K [4]). These results sparked tremendous interest and research on magnetic tunnel junctions, largely due to promising applications in recording read heads for hard disk drives and novel magnetic random access memories [6].
Theoretical background and experimental techniques

Figure 2.1: Typical TMR versus applied field curve for an exchange biased MTJ. Panel A shows an extended field range and the panel B shows the field range limited to the switching of the free layer. The direction of the magnetization of the free (blue arrow) and pinned layer (red arrow) is indicated in the graphs.

In order to be able to set the MTJs to the antiparallel magnetization state the two ferromagnetic layers must either have different coercive fields or one of them needs to be exchange biased. When a ferromagnet is grown onto an antiferromagnetic material the hysteresis loop is shifted or exchange biased with respect to zero field [7]. Both approaches have been successfully used in tunnel junctions while exchange biased MTJs are favored for applications which require reproducible switching characteristics [8]. Figure 2.1 shows a typical resistance versus applied field curve for an MTJ with an exchange biased bottom electrode (pinned layer). The relative field directions of the free (blue) and pinned layer (red) is indicated with arrows in the graph. The pinned electrode is exchange biased with a negative exchange biasing field. Panel A shows a sweep to sufficiently large magnetic fields to allow for the switching of both layers (major loop) while panel B only shows the reversal of the free layer (minor loop). The usefulness of the structure becomes apparent in panel B: two stable resistance states exist at zero applied field which differ in resistance by about 40%. The relative change in resistance, as indicated
2.1 Magnetic Tunnel Junctions

in figure 2.1, is defined as the tunneling magneto resistance (TMR)

\[ TMR = \frac{R_{AP} - R_P}{R_P} \]  

(2.1)

where \( R_{AP} \) and \( R_P \) denote the junction resistance for antiparallel and parallel alignment, respectively.

The TMR is highly dependent on temperature and applied bias. Increasing the temperature generally diminishes the TMR, most likely due to a reduction of the magnetic moment at the electrode interfaces by thermally excited spin waves [9]. The TMR generally decreases monotonically with applied voltage bias for bias voltages up to \( \sim 1 \text{ V} \) [10] but the voltage dependence can be asymmetric with respect to zero bias [11]. Moreover, zero bias anomalies are often observed [12].

After the initial success with using \( \text{Al}_2\text{O}_3 \) tunnel barriers a large variety of other barrier materials were investigated, e.g. \( \text{Ta}_2\text{O}_5 \) [13], \( \text{YO}_x \) [14], \( \text{ZrO}_x \) [15], and \( \text{HfO}_2 \) [16]. However, as yet none of these barriers are superior to \( \text{Al}_2\text{O}_3 \) in terms of TMR values. Recently, much effort was devoted to creating crystalline tunnel barriers like \( \text{ZnSe} \) or \( \text{MgO} \). In the course of this thesis highly textured MTJs using MgO barriers have been fabricated which show much higher TMR values than previously reported. These results as well as previous attempts to fabricate and measure single crystal MTJ structures will be discussed in chapter 4.

The first explanation for the tunneling magneto resistance effect was given by Julliere [1]. Based on the prior work of Meservey and Tedrow who had investigated tunneling between ferromagnetic and superconducting electrodes (see chapter 2.2), Julliere proposed that the TMR can be written as

\[ TMR = \frac{2P_1P_2}{1 - P_1P_2} \]  

(2.2)

with \( P_{1,2} \) being the spin polarization of the electrodes defined as

\[ P_{1,2} = \frac{|M_1|^2 N_1 - |M_1|^2 N_1}{|M_1|^2 N_1 + |M_1|^2 N_1} \]  

(2.3)
Here the tunneling matrix elements $|M_{\uparrow,\downarrow}|^2$ denote tunneling probabilities for tunneling of spin up and spin down electrons respectively and $N_{\uparrow,\downarrow}$ the corresponding density of states at the Fermi energy. The spin polarization $P_{1,2}$ can be measured directly using superconducting tunneling spectroscopy (see chapter 2.2) and is then referred to as tunneling spin polarization (TSP). The TMR values calculated from the TSP using equation 2.2 usually are an upper bound for the measured ones at low temperatures and zero applied bias. Julliere’s model allows calculation of the TMR if the spin polarization values are known. Theoretical calculation of these, however, has been proven to be challenging.

Given the shortcomings of Julliere’s model other models were proposed. Slonczewski calculated an approximate expression of the magnetoconductance of free electrons tunneling through a square barrier [17] based on the Landauer-Büttiker formalism. While this model takes into account some properties of the barrier it has been shown that the free electron approximation does not reproduce the tunneling of band electrons [18]. MacLaren has emphasized that a successful model needs to incorporate both the band structure of the electrons and the properties of the barrier [18]. Oleinik for example, has examined the electronic structure of the interface between Co and crystalline $\alpha$-Al$_2$O$_3$ [19] and finds that the spin polarization at the Fermi energy is very sensitive to the interface structure. Theoretically it is problematic to calculate tunneling currents for stacks containing disordered materials. Therefore, recently first principle calculations using fully epitaxial material systems were performed. These have shown features very different from Julliere type tunneling and will be discussed in chapter 4.

### 2.2 Superconducting tunneling spectroscopy

Using STS the TSP of a given FM/barrier combination can be measured. This method uses a superconducting counter electrode in an applied magnetic field as an analyzer for the spin polarized current.

Tunneling experiments involving superconductors (SC) were first carried out by Giaever in the early 60s [20, 21, 22, 23] followed by Shapiro [24]. Giaever used superconducting tunneling spectroscopy (STS) to measure the size of the
2.2 Superconducting tunneling spectroscopy

superconducting gap in various superconductors. He received the Nobel Prize for pioneering this technique in 1973 together with Esaki and Josephson [25].

2.2.1 Theoretical background

Assuming a tunnel junction with either superconducting or normal electrodes the Fermi levels in both electrodes will be equal. An applied bias voltage will shift the Fermi energy levels with respect to each other and lead to a tunneling current. This current, according to Fermi’s golden rule will be given by a product of the density of states (DOS) of filled states of a given energy in one electrode and the density of empty states in the other electrode at the same energy multiplied by the square of the matrix element ($|M|^2$) describing the tunneling probability. Usually this matrix element is taken to be independent of energy [26]. For low applied bias voltages the barrier height can be taken to be independent of applied bias. This approximation is justified in the case of STS and conventionally used tunnel barriers (Al$_2$O$_3$ and MgO) as applied biases are 3 orders of magnitude lower than the barrier heights. Using this model the current of electrons flowing at energy $E$ from electrode 1 to 2 is:

$$I_+(V, E) \sim N_1(E + eV)N_2(E)|M|^2 f(E + eV)[1 - f(E)]$$  \hspace{1cm} (2.4)

Here $V$ is the voltage on the first electrode with respect to the second, $N_1$ and $N_2$ are the densities of states of the first and second electrodes, $e$ is the absolute value of the electron charge, $f$ is the Fermi function and the energy $E$ is measured from the Fermi energy. The tunnel current from electrode 2 to electrode 1 is given by

$$I_-(V, E) \sim N_1(E + eV)N_2(E)|M|^2 [1 - f(E + eV)]f(E)$$  \hspace{1cm} (2.5)

And the total current ($I$) is $I_+ - I_-$ integrated over all energies (assuming that $|M|^2$ is independent of energy)

$$I(V) \sim |M|^2 \int_{-\infty}^{\infty} N_1(E + eV)N_2(E)[f(E + eV) - f(E)] dE$$  \hspace{1cm} (2.6)
Different cases can now be considered. If the two electrodes are non-magnetic metals the density of states can be taken to be constant for small applied biases. Then equation 2.6 reduces to

\[ I(V) \sim |M|^2 N_{n1} N_{n2} \int_{-\infty}^{\infty} f(E + eV) - f(E) \, dE \quad (2.7) \]

\( N_n \) here denotes the density of states in the normal metal. For small applied voltages it follows that \( I \sim V \).

If one of the electrodes is superconducting the integration over its density of states has to be carried out. Writing \( N_s \) for the density of states in the superconductor one can simplify equation 2.6 to

\[ I(V) \sim |M|^2 N_n \int_{-\infty}^{\infty} N_s(E) [f(E + eV) - f(E)] \, dE \quad (2.8) \]

It is convenient to calculate the conductance which in this case is

\[ \frac{dI}{dV}(V) \sim |M|^2 N_n \int_{-\infty}^{\infty} N_s(E) f'(E + eV) \, dE \quad (2.9) \]

where \( f' \) is the derivative of the Fermi function with respect to \( V \). At low temperatures \( f' \) approaches the \( \delta \) function and a measurement of the conductance closely resembles the density of states in the superconductor. This behavior is illustrated in figure 2.2 where for the sake of simplicity a BCS density of states is used. The power and directness of the measurement lies in being able to map out the density of states in the superconductor directly by measuring the conductance.

Giaever used the STS technique to probe the superconducting state. In 1970 Meservey and Tedrow observed a magnetic field splitting of the quasiparticle density of states in superconducting aluminum films [28]. They realized that the spin-split DOS of the superconductor in an applied field could be used to measure the spin polarization of the tunneling current from a ferromagnetic metal. First measurements were carried out using ferromagnetic Ni, an Al superconductor and an Al₂O₃ barrier [29]. For a review of the historical development and summary of
2.2 Superconducting tunneling spectroscopy

Figure 2.2: Cartoon illustrating the connection between superconducting DOS and measured conductance in a normal metal / superconductor junction. Panel (a) shows the BCS density of states in a superconductor. In panel (b) the temperature dependent derivative of the Fermi function in the integral expression for the conductance (equation 2.9) is depicted and panel (c) shows the resulting normalized conductance (from [27]).

For the case of tunneling between a ferromagnet and a superconductor equation 2.9 has to be modified to account for the fact that the conductance is the sum of contributions of the spin up and spin down channels. The matrix elements (|M|^2) can be different for tunneling of spin up and spin down electrons but are still taken to be independent of applied voltage. The superconducting density of states (N_s)
is now also a function of the applied field $H$. Thus equation 2.9 can be written as

$$
\frac{dI}{dV} \sim N_\uparrow |M_\uparrow|^2 \int_{-\infty}^{\infty} N_{s\uparrow}(E, H) f'(E + eV) dE
$$

$$
+ N_\downarrow |M_\downarrow|^2 \int_{-\infty}^{\infty} N_{s\downarrow}(E, H) f'(E + eV) dE \quad (2.10)
$$

Here $N_{s\uparrow\downarrow}$ is the spin up (down) density of states in the superconductor. Using this expression a measurement of $dI/dV$ allows the determination of the spin polarization of the tunneling current (TSP) which is given by

$$
TSP = \frac{|M_\uparrow|^2 N_\uparrow - |M_\downarrow|^2 N_\downarrow}{|M_\uparrow|^2 N_\uparrow + |M_\downarrow|^2 N_\downarrow} \quad (2.11)
$$

Figure 2.3 illustrates the superconducting density of states in a magnetic field (panel a) as well as the conductance of a FM/barrier/SC junction. Note the Zeeman split DOS in the SC with the spin up and spin down DOS peaks which are displaced by $2\mu_B H$. The conductance curve now has four peaks with the peak height being antisymmetric with respect to zero bias. The magnitude of this asymmetry is a measure for the spin polarization in the ferromagnet.

In figure 2.3 the BCS density of states is shown for both spin channels but displaced in energy due to the applied magnetic field. In the BCS theory, neither depairing due to the applied field nor spin-flip scattering are included. However, in the early experiments the BCS density of states was used to solve equation 2.10 and the TSP was calculated from the height of the four peaks in the conductance curve [27, 30]. Later, spin orbit scattering and orbital depairing in the superconductor were taken into account by using the DOS as derived by Maki [31, 32]. Following Maki the DOS can be written as

$$
N_{s\uparrow\downarrow}(E) = \frac{N_s(0)}{2} \text{sgn}(E) \text{Re}\left(\frac{u_\pm}{(u_\pm^2 - 1)^{1/2}}\right) \quad (2.12)
$$

where $u_+$ and $u_-$ are implicitly given by

$$
u_\pm = \frac{E \mp \mu_H}{\Delta} + \frac{\zeta u_\pm}{(1 - u_\pm^2)^{1/2}} + b\left(\frac{u_\pm - u_\mp}{(1 - u_\pm^2)^{1/2}}\right) \quad (2.13)$$
2.2 Superconducting tunneling spectroscopy

Figure 2.3: Cartoon illustrating the connection between superconducting DOS and measured conductance in a ferromagnet / superconductor junction in an applied magnetic field. Panel (a) shows the BCS density of states in a superconductor. In panel (b) the temperature dependent kernel in the integral expression for the conductance (2.10) is depicted (weighted with spin dependent DOS and matrix elements in the ferromagnet) and panel (c) shows the resulting normalized conductance (from [27]).

Here ∆ is the energy gap, \( N_s(0) \) is the normal density of states, \( \zeta \) is the orbital depairing parameter and \( b \) is the spin-orbit scattering parameter [33]. Fermi liquid effects as considered by Alexander [34] are not included as the measurements are usually performed well below the superconducting transition temperature where there are few quasi particles.

Solving equation 2.12 will allow a calculation of a theoretical conductance curve that allows for fitting of the experimental data. If the temperature and applied field are known the remaining fitting parameters are the superconducting gap (∆), depairing parameter (ζ), spin orbit parameter (b) and the spin polarization of the tunneling current (\( TSP \)). A discussion of how to solve equation 2.12 was given by...
2.2.2 Orbital depairing and spin orbit scattering in superconductors

It is not intuitively obvious that an applied field would lead to a Zeeman splitting of the quasiparticle density of states in a superconductor. Due to the Meissner effect [36] a superconductor in a magnetic field responds by screening the field by establishing circulating currents similar to eddy currents in a normal metal. However, if the thickness $d$ of the superconductor is much smaller than the penetration depth of the field ($\lambda$) then a field applied parallel to the plane of the film can penetrate it almost uniformly. Maki [37] showed that in the short-mean-free-path limit the the strength of the interaction detrimental to superconductivity can be included in terms of the depairing parameter $\zeta$ with

$$\zeta = \frac{e^2 d^2 v_F l H^2}{18 \hbar} \quad (2.14)$$

Here $v_F$ denotes the Fermi velocity, $l$ is the mean free path, and $H$ the magnetic field applied in the film plane. Thus in the short mean free path limit and for thin films the critical field is large. However, Meservey and Tedrow showed that for very thin films ($<100 \text{Å}$) the critical field is determined by Pauli paramagnetism [38, 27]. Pair breaking can not only be caused by an applied magnetic field but also by magnetic impurities in the SC. Figure 2.4 illustrates the influence of a change in $\zeta$ on the superconducting DOS.

In contrast to magnetic impurities non–magnetic impurities cannot break pairs but lead to spin flip scattering. Abrikosov and Gorkov calculated the strength of this process and and found that the scattering rate $\tau_{so}^{-1}$ varies as $\tau^{-1}$, as follows

$$\tau_{so}^{-1} \sim \left( \frac{e^2 Z}{\hbar c} \right)^4 \tau^{-1} \quad (2.15)$$

Here $Z$ is the nuclear charge and $1/\tau$ the rate of momentum scattering. In Maki’s description of the superconducting DOS the normalized spin-orbit scattering rate

Worledge [35].
Figure 2.4: Influence of orbital depairing parameter ($\zeta$) on the theoretical conductance curve in a normal metal / barrier / superconductor junction. The curves are calculated using an applied field of 2 T, a temperature of 0.25 K and a spin-orbit scattering parameter of 0.03. The values of $\zeta$ used are indicated in the graph.

$b = \hbar/3\Delta\tau_{so}$ is used. The modification of the spin-dependent density of states of excited quasiparticles was pointed out by Engler and Fulde [39]: With increasing $b$, the two outside peaks are decreased relative to the inside peaks. For large $b$, the superconductor behaves as though the quasiparticles had no spin [40]. This behavior is illustrated in figure 2.5 where only the conductance for positive applied bias is shown. Note that $b$ is proportional to $Z^4$. Thus for superconductors with high nuclear charge no spin effects will be observed due to strong spin orbit scattering.

The above discussion shows that in order to observe any spin effects the superconducting layer needs to be sufficiently thin to reduce the depairing and should be a material with low $Z$. Furthermore, in order to perform the experiment, one needs to be able to interface it to the insulating barrier material. Al has proven to be the material of choice, not only because of its low inherent spin orbit scattering rate but also due to the fact that its native oxide is self limiting in the thickness range useful for planar tunnel junctions. A thin layer of Al ($\sim50\text{ Å}$) can have a
Theoretical background and experimental techniques

2.2.3 Fitting procedure

Figure 2.5: Influence of the spin-orbit scattering parameter \( b \) on the theoretical conductance curve in a normal metal / barrier / superconductor junction. The curves are calculated using an applied field of 2 T, a temperature of 0.25 K and a depairing parameter of 0.01. The values of \( b \) used are indicated in the graph.

Historically the thin Al layer was deposited at cryogenic temperatures to promote the growth of flat layers [32]. Later, small amounts of impurities (Cu [41], Si [42] or oxygen [43]) were used to prevent hillocking. These impurities reduce the mean free path and thus increase spin orbit scattering in the SC but also decrease the effect of pair breaking due to the applied magnetic field.

critical field determined by the Pauli paramagnetic limit in excess of 5 Tesla and a critical temperature that is raised from its bulk value (~1.2 K) to above 2.6 K.
parameters are $\zeta$, $b$, $\Delta$ and the tunneling spin polarization. In the fitting procedure these parameters are adjusted until the theoretical curve fits the experimental one well.

Figure 2.6: Experimental conductance curve at 2 T (black dots in panel a) and 5.5 T (blue dots in panel a) as well as 2 T data with the background subtracted (black dots in panel b). The red line in both panels indicates the theoretical fit.

Figure 2.6 shows experimental conductance curves for 2 T and 5.5 T applied field. At 5.5 T the superconductivity is quenched and the conductance should be constant for the small applied voltage range. However, evidently the data shows some non–ohmic behavior, probably due to well known zero bias anomalies in tunnel junctions [12]. The raw conductance data cannot be fitted properly over the whole voltage range due to this non-ohmic background. After subtracting the background the data can be fitted very well (see figure 2.6 panel b). The
background can be determined by driving the SC normal either by applying a field higher than the critical field or increasing the temperature above the Curie temperature. Although there are four fitting parameters the TSP can be extracted with high accuracy (±1%) as the asymmetry of the low energy peaks, which is a measure of the spin polarization, is largely insensitive to changes of $\Delta$, $b$, and $\zeta$.

Figure 2.7: Conductance versus applied voltage for Al$_{96}$Si$_4$/Al$_2$O$_3$/Ho junction (open circles). The solid lines indicate theoretical curves using two different magnetic fields. Although the applied field was 2 T the fit using 2.9 T (red line) fits the data much better than the fit using 2 T (blue line).

Although the applied field $H$ and temperature $T$ are usually set to the measured values and not adjusted in the fitting procedure there are cases where the values needed for a proper fit deviate from the measured ones. An example is shown in figure 2.7 where the conductance curve for the following sample is shown:

45Å Al$_{96}$Si$_4$ | 14Å Al – 240s plasma oxidization | 300Å Ho | 100Å Ta

The applied field during the measurement was 2 T. In figure 2.7 the experimental data as well as fitting curves for 2.9 T and 2 T applied field are shown. Evidently
the fitting curves indicate that the actually applied field was much higher than 2 T. This additional Zeeman splitting is induced by the Ho layer. This exchange proximity has been observed in the past for Al in contact with rare-earth oxides [45, 46, 47] and metals [48, 30].

2.2.4 Spin polarization values obtained with STS

Since the early 70s the spin polarization of a large variety of materials was measured. Meservey and Tedrow determined the TSP of Co, Fe and Ni as well as alloys of these elements. The results are shown in figure 2.8 together with TSP data from Monsma [41] and Slater-Pauling curves from [49]. The TSP is measured to be positive for Co, Fe and Ni as well as all their alloys. Monsma’s values are slightly higher than Meservey’s which can be attributed to improved sample preparation. Ni and Ni rich alloys seemed to have a low TSP as compared to Fe and Co rich alloys, probably due to problems in creating a high quality interface to the barrier [50]. However, recent experiments show that a TSP for Ni can be obtained that is similar to the one of Co and Fe [51, 52].

Paraskevopoulos measured the spin polarization of alloys comprised of the ferromagnetic 3d transition metal alloys and the paramagnetic elements Cr, Cu, Mn and Ti [53]. He found an approximately linear relationship between magnetization and spin polarization. However, it has been pointed out that magnetization and spin polarization have very different physical origin and that this proportionality seems to be accidental. This was illustrated by measuring the composition dependent spin polarization of Co-Pt and Co-Pd alloys [54, 50].

After the initial measurements many more materials have been measured, including rare–earth metals, Heusler alloys, and perovskites. Much attention was focused on materials which were predicted to be half metallic (NiMnSb, CrO₂, Fe₃O₄, and LSMO). Table 2.1 shows a compilation of experimental results for different materials together with the insulating barriers used and references.

Evidently superconducting tunneling spectroscopy could not verify the half metallic nature of LSMO and NiMnSb. However, because the calculations that predict half metallic behavior are performed for the bulk the applicability for the case of thin layers and the interface sensitive tunneling process is not evident.
The theoretical background and experimental techniques

Figure 2.8: Tunneling spin polarization and magnetic moment per atom for different Co-Fe and Ni-Fe alloys. TSP data from Meservey [30, 53] and Monsma [41] are shown for comparison. The Slater Pauling curves are taken from [49].

The same holds for polarization measurements using Andreev reflection [58, 59]. Another problem arises with preparation of high quality interfaces (i.e. for the case of NiMnSb the interface to the barrier is likely to be MnSb rich [60]).

The TSP of Fe$_3$O$_4$ cannot easily be determined at low temperatures because it undergoes a Verwey transition at $\sim$ 120 K and a gap in the minority density of states is opened up at lower temperatures [61]. However, it is still possible to measure the TSP which is then determined by spin filtering and hopping conductance through

<table>
<thead>
<tr>
<th>Material</th>
<th>TSP</th>
<th>Barrier</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrO$_2$</td>
<td>&lt;95%</td>
<td>Cr$_2$O$_3$</td>
<td>[55]</td>
</tr>
<tr>
<td>La$<em>{0.67}$Sr$</em>{0.33}$MnO$_3$</td>
<td>+72%</td>
<td>SrTiO$_3$</td>
<td>[43]</td>
</tr>
<tr>
<td>SrRuO$_3$</td>
<td>-9.5%</td>
<td>SrTiO$_3$</td>
<td>[56]</td>
</tr>
<tr>
<td>NiMnSb</td>
<td>+28%</td>
<td>Al$_2$O$_3$</td>
<td>[57]</td>
</tr>
</tbody>
</table>

Table 2.1: Compilation of TSP values for different ferromagnetic materials
the Fe$_3$O$_4$ layer. Using an Al$_2$O$_3$ barrier a maximum TSP of $-48\%$ has been measured [62, 63]. Similar spin filtering effects have also been observed using EuO [64] and EuSe [65] barriers.

2.3 Sample preparation

All the samples described in the work were grown in deposition systems built and operated in Stuart Parkin’s group at the IBM Almaden Research Center. Two different deposition chambers (A– and S–system) were used which have many features in common. Both chambers are equipped with multiple DC magnetron sputter guns and a plasma oxidization source. Additionally the A–system is equipped with two effusion cells, an ion beam sputter source with a five target turret and an electron-beam evaporation source.

![Schematic of the sputtering system](image)

The chambers have a base pressure of better than 10$^{-9}$ Torr. A critical feature of both systems is the use of multiple substrates (20 for the S-system and 24 in the A–system) and the capability of shadow masking (up to eight different masks
can be used in a run). The shadow masks are used to define patterns of the deposited material on the substrate. They are made of copper–beryllium and can be fabricated to allow for feature sizes down to 20 µm. However, for MTJs and STS structures usually the smallest features were about 80 µm. Both the substrate and mask platters are independently rotatable, thus allowing for use of any substrate with any mask at any gun position (see figure 2.9 for a schematic drawing of the S–system). Permanent magnets placed above the substrate platter in several of the deposition positions create a ∼100 Oe magnetic field used to set the exchange bias direction.

The deposition system is fully automated. Thus the films are grown under computer control after the sample structures have been specified by the user. This allows for very reproducible films and for growth of a large variety of samples in the shortest amount of time possible. Samples were grown on 1” diameter Si(100) wafers with 500 Å of thermally grown oxide on the surface. Typically, they are cleaned for ∼8 minutes in an ultra-violet ozone cleaning system and then rinsed in de-ionized water for 2 min. Afterwards they are placed for ∼2 min in the vapor from boiling isopropanol and then dried in a hot nitrogen drying tunnel. The clean substrates are then placed in the sputtering system. The deposition of 20 wafers with regular MTJ stacks takes about 8 hours. Then the chamber is vented, new substrates are loaded, targets are changed if needed, and the chamber is baked for about 8 hours prior to the next run.

Both deposition systems allow for deposition in argon, oxygen, nitrogen or any combination of the above. Usually the deposition of metals is done in an Ar atmosphere of 3 mTorr. Oxide barriers can either be fabricated by plasma oxidization of the metal (usually in 100 mTorr O₂) or via reactive sputtering of the metal in a Ar/O₂ atmosphere where the Ar/O₂ ratio is usually set between 97/3 and 90/10.

For a regular MTJ bottom and top electrodes are fabricated as two crossed stripes each about 80 µm wide. The barrier is deposited as a large rectangle which is much wider than the active area of the junctions. Figure 2.9 shows a cartoon of a deposited wafer (which consists of 3 bottom electrodes and 10 top electrodes thus defining 10 tunnel junctions), and an SEM picture of one junction.
2.3 Sample preparation

The STS samples are usually grown with the superconductor on the bottom (normal structure) – in this case the same mask combination as for the MTJs is used. However, when the structure is reversed and AlSi constitutes the top electrode, the junctions are then found to be shorted if a special mask combination is not used. An SEM picture of a junction grown with these masks is shown in figure 2.10. The top electrode is electrically insulated from the bottom one with two isolation pads located under the top electrode. The distance between the pads and the width of the top electrode then defines the active area of the junction.

All the masks have special rectangular cutouts along two sides which leads to two 2 mm × 6 mm rectangular areas on the substrates which contain the full film structure and the film stack up to the barrier, respectively. These areas can be used for further analysis, e.g. via Transmission Electron Microscopy (TEM).

The deposition rates of the different materials are on the order of 1 Å/s. To determine the rates, 500 Å thick calibration films are deposited on specially masked substrates. The mask for the calibration films allows thickness measurements with a DekTak mechanical profilometer. After the thickness of the film is determined the deposition rate can be calculated. Also, the calibration films can be analyzed with Rutherford Back Scattering Spectroscopy (RBS) to determine the composition of alloy films (using sputtering the target composition is not always mapped 1:1 onto
the substrate) as well as impurity concentrations and thickness of the film.

Using fully automated sputtering systems which employ shadow masking leads to a quick turnaround time and enables the fabrication of a large amount of samples in a short amount of time. Only for the superconducting tunneling spectroscopy measurement more than 110 runs were performed which amount to about 2200 samples each of which is unique in material combination, layer thicknesses etc. Although not all of these samples could be measured at low temperatures it allowed for quick optimization of sample structures and investigation of material properties.
Chapter 3

Rare Earth – Transition Metal alloys in tunneling structures

3.1 Introduction

As outlined in the previous chapters, the working principle of spintronic devices such as spin valves or magnetic tunnel junctions is based on the inherent spin imbalance in ferromagnetic materials. In conventional devices the ferromagnetic 3d transition metals (Co, Fe, and Ni) have predominantly been used because of their ease of fabrication, high Curie temperatures and well understood magnetic properties [6]. Equally important, using exchange bias [7] and oscillatory interlayer coupling [66] thin film structures of transition metals can be magnetically engineered to create useful devices. Moreover, the material properties (e.g. saturation magnetization, coercivity, and anisotropy) can be tailored by alloying Co, Fe, and Ni with other ferromagnetic or non–magnetic elements (Co$_{70}$Fe$_{30}$ is typically used in this thesis for the MTJ electrodes as its spin-polarization significantly exceeds the polarization of Co or Fe metal [41] and gives rise to more thermally stable devices). Studying the spin polarization not only of Co, Fe and Ni but also of alloys of these elements with paramagnetic transition metals gives important insight into the nature of spin–dependent tunneling. For example, the importance of tunneling matrix elements is nicely illustrated in the variation of Co-Pt spin polarization with increasing Pt composition [50].
While the spin–dependent transport properties of ferromagnetic transition metal alloys with paramagnetic 3d, 4d and 5d elements have been studied for many years much less attention has been focused on alloys of Co, Fe and Ni with the ferromagnetic 4f elements (rare earth – transition metal alloys). These materials display a wide variety of unique properties such as ferrimagnetic ordering, amorphous structures and perpendicular magnetic anisotropy in thin films that cannot be found in conventional materials and which make them promising candidates for magneto–optical storage media. For these applications, the amorphous structure (which reduces the grain noise), tunable Curie temperature (which enables Curie point writing [67, 68]) and perpendicular anisotropy [69] are most important. Thus, much attention has been focused on Co-Fe-Gd-Tb alloys with perpendicular anisotropy and a Curie temperature above room temperature.

In this chapter, rare earth – transition metal (RE-TM) alloys will be discussed emphasizing properties important for their use in MTJs. The spin polarization of RE-TM alloys has been measured directly using STS at low temperatures (chapter 3.3) as well as at elevated temperatures using MTJ stacks (chapter 3.4). Using a Co-Fe interlayer between barrier and electrode the TMR can be significantly enhanced (chapter 3.5). The high TMR, together with high thermal stability (chapter 3.5.2) and suitable magnetic anisotropy (chapter 3.7) illustrates the potential use of these materials in applications. A double tunnel junction structure that makes use of the unique properties of RE-TM alloys is described in chapter 3.6.

3.2 Material Properties

The materials under investigation here are alloys between the rare-earths (elements of the lanthanide series) and ferromagnetic transition metals (Co, Fe and Ni). The magnetic properties of the rare earths are dominated by a partly filled 4f shell which can result in very high magnetic moments per atom. The exchange in RE metals is mediated by the 4s–5d conduction electrons via the RKKY interaction. The Curie temperatures for the ferromagnetic RE metals are much lower than
those of the 3d based ferromagnet, Gd is the only element in the series which is ferromagnetic at temperatures close to room temperature.

Films of the RE-TM alloys can be prepared so that they are either crystalline or amorphous. Various deposition methods have been used to create amorphous films including sputtering, thermal evaporation, and liquid quenching. The crystallization temperatures are well above room temperature (see [70] for a compilation of experimentally measured crystallization temperatures). Figure 3.1 shows the phase diagram of Co-Gd. Note that a wide range of intermetallic compounds is present.

![Figure 3.1: Co-Gd phase diagram (from [71])](image-url)
When alloyed with the 3d ferromagnetic elements Co, Fe or Ni the RE elements retain their high moments even at higher temperatures than the Curie temperature of the pure RE metals. In fact, the early research on RE-TM alloys was geared towards the use of these elements in permanent magnets [72] by combining the high Curie temperature of the TM with the high moments of the RE elements. For this application the light RE elements are used because these couple ferromagnetically with the TM elements giving rise to high magnetization. By contrast the heavy rare earths (Gd to Lu) couple antiferromagnetically to the TM moments thereby reducing the net moment. This can be simply understood from Hund’s rule. Hund’s rule states that for less than half filled shells the orbital moment and spin moment couple antiparallel \((J=L-S)\) while they couple parallel \((J=L+S)\) in the second half of the series. As the orbital moment is always greater than the spin moment for the light RE elements the total moment is antiparallel to the spin moment. Because the 4f spin moment couples antiparallel to the TM moment (mediated through positive 4f-5d and negative 5d-3d exchange [73]) the total moment on the RE couples parallel to the TM moment for the light REs and antiparallel for the heavy REs. The relative orientation between spin and orbital moments is schematically illustrated in figure 3.2.

![Figure 3.2: Relative orientation of spin and orbital moments for alloys between transition metals (TM) and light and heavy rare earths (RE)](image)

It follows from the above discussion that alloys between light RE and TM are ferromagnets while alloys between heavy RE and TM are ferrimagnets. However, in amorphous alloys, the situation is a bit more complicated than depicted in the
3.2 Material Properties

cartoon in figure 3.2. Because the local easy magnetic axis for the magnetization varies randomly from site to site due to variations in the local crystalline fields, the moments will be canted with respect to moments of the same or the other elements [74]. This randomizing of the orientation of the magnetic moments is opposed by the exchange interaction which favors parallel alignment. Some typical spin structures, observed in experiments, are depicted in figure 3.3. Gd based alloys show a collinear structure as Gd has no orbital moment and thus no significant crystalline anisotropy. For Co-Dy and Co-Nd the RE subnetworks are canted with respect to the Co moments which are parallel to each other due to the Co-Co exchange coupling.

The magnetization on the RE (or TM) atoms add up to a so-called RE (or TM) subnetwork magnetization. Here the term subnetwork magnetization is used rather than sublattice magnetization because of the amorphous structure. The combination of both the RE and TM subnetwork magnetizations add up to the net magnetization.

![Figure 3.3: Classes of magnetic structures found in RE-TM alloys](image)

The ferrimagnetic ordering leads to an interesting dependence of the magnetization on composition and temperature for alloys between transition metals and heavy rare earths. Figure 3.4 shows composition dependence of the net magnetization at 4.3 K in Co-Gd and Fe-Gd alloys (from [75]). At around 20 atomic % of Gd, the Co and Gd subnetworks cancel each other out thus leading to zero net moment in the alloy (this composition is called the compensation composition). The larger Fe moment means that the compensation point is at a higher Gd content (∼2%).
A similar compensation behavior can be seen in the temperature dependence of the magnetization (see figure 3.5). The Gd subnetwork magnetization is more strongly temperature dependent than the Co subnetwork magnetization so that the relative magnitude of the subnetwork magnetizations changes with temperature. In figure 3.5 one can also see that the addition of Gd reduces the Curie temperature of the alloy due to reduced Co-Co exchange interaction. The dependence of magnetization on composition is shown here for Co-Gd but is very similar for alloys of Co, Fe, or Ni and the heavy RE elements from Gd to Yb, all of which have a ferri- or sperimagnetic structure [76].
3.3 Tunneling Spin Polarization of RE-TM alloys

Superconducting tunneling spectroscopy has been an important tool in determining the spin polarization of a wide variety of magnetic materials since it was first introduced in the early 70s [29]. With the exception of magnetite (Fe$_3$O$_4$) [63] and SrRuO$_3$ [56] all materials under investigation have so far been measured to be positively spin polarized (i.e. the tunneling current is dominated by majority spin polarized electrons). These include the ferromagnetic elements Co, Fe, Ni, Gd, Tb, Dy, Ho, Er, Tm, alloys of these elements with various paramagnetic transition metals (e.g. V, Ru, Pt, and Pd), as well as more complex materials such as CrO$_2$ [55], Heusler alloys (e.g. NiMnSb [57]) and Perovskites (e.g. LSMO [77]). See chapter 2.2.4 for a more detailed discussion of these results.

In this chapter results will be shown for the spin polarization of RE-TM alloys. These show negative spin polarization for certain composition ranges. The
mechanism here is quite different from the mechanism that leads to the negative TSP of Fe$_3$O$_4$ as will be explained later in this chapter. Understanding this mechanism is important for understanding spin polarized tunneling in general, but also has some technological importance. In particular, the properties of certain tunnel based devices can be improved by using both positively and negatively spin polarized materials.

Figure 3.6 shows our first observation of negative TSP for a RE-TM alloy (here Co$_{58}$Tb$_{42}$).

![Figure 3.6: STS conductance curve for a Al$_{96}$Si$_4$/Al$_2$O$_3$/Co$_{58}$Tb$_{42}$ junction.](image)

The conductance versus voltage curve looks similar to positively spin polarized materials in the normal structure (n-FIS) but is reflected around zero bias. As outlined in chapter 2.3, normal structure (n-FIS) means that the SC forms the bottom electrode while it is on top in the inverted structure (i-FIS) [42]. See figure 3.7 for an illustration of the different structures. We use the voltage convention that the bottom electrode is always positively biased. Thus reversing the structure would lead to a mirror–imaged curve. The same effect would be seen if one replaces a positively polarized electrode with a negatively polarized one but keeps the
structure otherwise the same. Thus a material with negative TSP in the n-FIS structure looks similar to a positively polarized one in the inverted structure.

Figure 3.7: Cartoon of normal (n-FIS) and inverted (i-FIS) structures for STS measurements

Figure 3.8 shows the TSP measured at 0.25 K and 2 T for various Co-Gd alloys. Results for several different structures are shown in the graph. The blue bullets (●) have Al$_2$O$_3$ barriers and are fabricated in the normal structure. Green circles (○) indicate MgO barriers in the normal structure while the red squares (□) indicate MgO barriers in an inverted structure. The exact structures are as follows:

- 45Å Al$_{96}$Si$_4$ | 14Å Al | plasmaox. | 300Å Co$_{1-x}$Gd$_x$ | 100Å Ta (n-FIS)
- 45Å Al$_{96}$Si$_4$ | 25Å MgO | 300Å Co$_{1-x}$Gd$_x$ | 100Å Ta (n-FIS)
- 100Å Ta | 250Å Ir$_{78}$Mn$_{22}$ | 35Å Co$_{1-x}$Gd$_x$ | 25Å MgO | 60Å Al$_{96}$Si$_4$ (i-FIS)

The Al and MgO thickness are varied by a few Å for different samples. The plasma oxidization time for the Al film was usually varied from 180s to 300s. In the inverted structure we use a set of standard Ta/IrMn underlayers. Usually the IrMn layer is used in MTJs to exchange bias the bottom electrode while the Ta layer is a seed layer to promote proper growth of the IrMn layer. Here the exchange biasing does not play a role as the samples are measured in a 2 T magnetic field (much higher than the exchange bias field which is around 200 Oe). The Co-Gd layer is prepared by sputtering from an alloy target of the desired composition. This target composition is not mapped 1:1 onto the substrate because sputtered Co and Gd atoms are scattered from the Ar atoms in the vacuum chamber at different rates due to their relative masses relative to argon. More Co than Gd is
scattered away from the substrate leading to higher Gd contents in the film. Thus, sputter power and argon pressure during deposition influence the composition of the deposited film. The composition in the deposited films was measured using Rutherford Back Scattering Spectroscopy (RBS) on ∼500Å thick unpatterned films of Co-Gd which were deposited in the same run as the samples for the STS experiments and protected from oxidation by 100Å of Ta on top and bottom. In figure 3.8 the compositional values measured by RBS are used rather than the nominal composition of the target. A more detailed description of sample preparation can be found in chapter 2.3. The four data points around 20 atomic % Gd are measured for Co-Gd alloys of nominally the same composition but are from different samples which were fabricated in the same run. Those samples had different plasma oxidation times to form the Al₂O₃ tunnel barrier but were otherwise identical.
3.3 Tunneling Spin Polarization of RE-TM alloys

Figure 3.9 shows the conductance versus voltage curves for junctions using Co-Gd alloys of selected composition ratios from figure 3.8. The structure of the samples is indicated with either n-FIS (normal structure – SC is bottom electrode) or i-FIS (inverted structure – SC is top electrode). The data are indicated by open circles and the fits are shown as solid lines which fit the data very well. The value for the tunneling spin polarization can be extracted with an accuracy of ±1%.

Magnetic tunnel junctions usually show a pronounced increase of TMR on annealing (in a magnetic field). The STS samples with Al$_2$O$_3$ barriers and conventional electrodes like Co$_{70}$Fe$_{30}$ do not display an increased TSP while the TSP for MgO based junctions is greatly enhanced upon annealing (see chapter 4). The samples with Co-Gd do not show either behavior. Here annealing leads to a decrease in TSP together with a decrease in resistance. The reason is the reactivity of the Co-Gd alloys which likely pulls oxygen from the barrier [78, 79, 80].

From figure 3.8 it can be seen that Co metal and Gd metal have a TSP of +42% and +13% respectively which is the same within experimental uncertainty as results previously obtained [30, 81, 82, 41]. The results show that from about 20 to 80 atomic % Gd the TSP is negative, peaking at about −30% for Co$_{70}$Gd$_{30}$. The results for MgO and Al$_2$O$_3$ barriers are qualitatively the same with the samples using MgO barriers in the inverted structure having higher negative TSP as compared to their counterparts in the normal structure.

The TSP data for Co-Gd alloys are very different from those for alloys of Co, Fe and Ni with paramagnetic transition metals. Early on Meservey and Tedrow measured the TSP of Ni alloyed with Fe, Mn, Cr and Ti. Their data supports the conclusion that there is a linear relationship between magnetic moment and TSP [81]. We investigated alloys of Co and Fe with V, Ru, Pt and Pd and while a linear relationship holds for V and Ru, a more complex behavior is found for Pt and Pd solutes [54]. For none of these alloys negative TSP is observed, though. In the light of these previously measured alloys the above results for Co-Gd alloys are striking.
Figure 3.9: Conductance versus voltage curves for selected STS junctions with various Co-Gd compositions.

RE-TM alloys have an important distinction as compared to alloys of Co and Fe with paramagnetic solutes as the RE elements possess a magnetic moment. As explained before changing the composition changes the relative magnitude of the subnetwork magnetizations. To verify that the STS samples indeed show this behavior the saturation magnetization of Co-Gd alloys of various compositions close to the compensation point were measured. The magnetization was measured at 10 K on small pieces of calibration films deposited in the same runs as the STS samples using a SQUID magnetometer. The saturation magnetization was determined by extrapolation to zero field of the moment versus field at high fields up to 5 T. These samples were typically \( \sim 500 \) Å thick. The actual thickness was determined from mechanical profilometry. With magnetization, area and thickness the volume magnetization can be determined. Figure 3.10 shows the result. The solid line corresponds to data from the literature [75] while the blue dots represent our
3.3 Tunneling Spin Polarization of RE-TM alloys

Figure 3.10: Composition dependence of saturation magnetization of Co$_{1-x}$Gd$_x$ alloys measured with a SQUID magnetometer at 10 K (blue dots). For comparison, the plot also shows data from ref. [75] (solid line). The compensation point inferred from these measurements agree well with the literature data.

A cartoon of the relative orientations of the RE and TM subnetwork magnetizations is shown in figure 3.11 where the magnitude and direction of the subnetwork magnetization is drawn for various Co-Gd compositions.

At the compensation point (~Co$_{80}$Gd$_{20}$) the net magnetization vanishes (not indicated in the cartoon is that here the orientation of the moments does not have a preferred direction with the applied field but will depend on the anisotropy, temperature history, magnetic field history etc.). For lower Gd concentrations the Co subnetwork magnetization is higher than that of the Gd subnetwork (thus the Co subnetwork is parallel to the applied field) while for higher Gd concentrations the relative orientation of the RE and TM moments to the applied field reverses.

This reversal in subnetwork magnetization directly implies a sign reversal of the TSP at the compensation point. This is simply due to the fact that the applied
field is the quantization axis and spin up and spin down are defined with respect to this axis (at the compensation point spin up electrons in one of the magnetic components become spin down electrons and vice versa). Similarly, one would observe a sign reversal in the measured TSP if one could reverse the magnetization of the ferromagnetic layer with respect to the applied field which Zeeman splits the superconductor quasi–particle DOS. This variation of orientation of the RE and TM moments with respect to the applied field explains why the TSP reverses its sign around 20 atomic % of Gd. In figure 3.8 there are multiple datapoints for Co$_{80}$Gd$_{20}$. They only differ in the plasma oxidization time used to form the Al$_2$O$_3$ barrier and thus in resistance. As the Co-Gd is deposited on top the Al$_2$O$_3$/Co-Gd interface is unchanged by the change in plasmaoxidization time. However, the samples show different TSP varying from +9% to -13%. Because the Co-Gd composition is exactly at the compensation point (the volume magnetization of the Co$_{80}$Gd$_{20}$ calibration film made in the same run was lower by a factor of 20 as compared to pure Co) slight changes in composition due to, for example, small variations in deposition conditions can have a dramatic effect and even change the sign of the measured spin polarization. However, the -13% TSP measured is likely to be a lower bound for the TSP that would be measured if all the moments (even at the interface) were perfectly aligned.

Even with the above explanation it is not intuitively obvious that at a composition very close to the compensation point (or right at the compensation point)
3.3 Tunneling Spin Polarization of RE-TM alloys
	here should be a sizable spin polarization because there the net magnetization vanishes. However, the above results prove that even in the case of vanishing net moment the tunneling electrons can be sizably polarized due to the fact that the tunneling matrix elements for tunneling from different atoms are different and their relative polarization is different.

The second sign reversal of TSP at around 80 atomic \% Gd cannot be understood within the same framework above, since the relative orientation of the moments to the applied field remains unchanged around 80 atomic \% of Gd.

Calculating the TSP for any kind of material has been proven to be quite challenging in the past (see chapter 2). While first principles calculations have been successful in calculating the tunneling properties for crystalline systems they usually fail to correctly predict TMR or TSP magnitude and sign when amorphous insulating barriers are used. Furthermore, density of states (DOS) calculations combined with the Julliere model of tunneling [1] have failed to explain the TMR and TSP values measured in experiments. The reason for this is believed to be due to the fact that the tunneling probability for electrons in different bands can be quite different [83] (tunneling is dominated by itinerant electrons while the DOS close to the Fermi Energy in TM or RE is mainly from localized electrons). These tunneling matrix elements cannot readily be calculated. Thus the effect of alloying on the TSP cannot be easily quantified either. For some alloys (Co-Pt, Co-Pd, Fe-Pt, and Fe-Pd) a highly simplified but intuitively pleasing model can account for the experimental results, though [54]. Here the addition of the solute (Pt and Pd) does not change the magnetic moment on the Co atoms and the overall tunneling current can be seen as the sum of the tunneling current from either Co and Fe or Pt and Pd. As the Co moment is largely unchanged and the Pt only picks up a small magnetic moment of \(<0.3 \mu_B\) (this was determined by X-ray magnetic circular dicroism for Co_{65}Pt_{35} films) one can reasonably assume that the tunneling current from Co is 40\% polarized while that from Pt is unpolarized. Thus one can develop a simple model in which the overall TSP depends on the TSP of Co, the TSP of Pt, the composition as well as the tunneling probabilities for tunneling from the respective atom. This model thus gives the formula below which fits the
experimental data reasonably well.

\[ P = P_1 \frac{1 - x}{1 - x + x/r} + P_2 \frac{x}{x + (1 - x) \times r} \]
\[ r = \frac{r_1}{r_2} \]

Here \( P \) is the overall tunneling spin polarization measured for an alloy between element 1 and 2. \( P_1 \) and \( P_2 \) denote the polarizations of the pure elements 1 and 2, respectively, while \( x \) is the fraction of element 2 in the alloy. \( r_1 \) and \( r_2 \) are the tunneling rates for tunneling from element 1 or 2 respectively (thus \( r > 1 \) indicates that tunneling from element 1 is more probable as compared to element 2). This model is very simplistic and one might argue that it ignores the complex interplay between the density of states, tunneling matrix elements, and barrier shape etc. Nonetheless the model fits the Co-Pt data well and is likely applicable for other alloy systems as well where the local DOS of the ferromagnetic component is not much changed dramatically with composition.

If one applies the above model to the TSP of Co-Gd alloys a further complication enters the picture in that the relative orientation of the subnetworks changes with respect to the applied field at the compensation point. The reversal of the moments will lead to a reversal of the sign of the spin polarization for Gd concentrations higher than \( \sim 20 \) atomic %. Taking this into account one can fit the polarization data shown in figure 3.8 with equation 3.1. The resulting curve is shown in figure 3.8 as a dashed line. It fits the data well, except for compositions close to the compensation point.

The fitting parameters are \( \sim 40\% \) polarization for the Co atoms, \( \sim 13\% \) for Gd and a tunneling rate for Co 1.5 times higher than for Gd. From the previous work on Co-Pt and related alloys (Co-Pd, Fe-Pt, and Fe-Pd) one can conclude that bonding to the oxygen plays an important role in determining the tunneling rates. Since Pt is a noble metal, forming only weak bonds with oxygen while Co forms strong bonds we conclude that the tunneling rate for tunneling from Co is higher than from Pt (the experiments show, by a factor of 3). For the case of Co-Gd, Gd is believed to be preferentially oxidized (This was established for Co-Gd alloys
3.3 Tunneling Spin Polarization of RE-TM alloys

[78, 79, 80] as well as for compositionally modulated Co/Gd multilayers [84]. Similar results were obtained for Fe-Tb [85, 86] and Co-Fe-Tb [87]). Nevertheless, one finds that the tunneling rate for tunneling from Co is higher by a factor of 1.5 as compared to Gd. This shows that although the Gd is more likely to form oxygen bonds the tunneling current is dominated by electrons tunneling from Co. This in conjunction with the fact that the magnetic moment on the Gd atoms (∼7.5 $\mu_B$) is much higher than that on the Co (∼1.7 $\mu_B$) is the reason that high negative TSP can be achieved. The magnetization values here are for pure Gd and pure Co.

While the moment on the Gd stems from highly localized 4f electrons the moment on the Co atoms rather depends on the detailed structural and chemical environment and on hybridization effects. Following this line of argumentation, Hansen deduced the average magnetic moment on the Co sites upon alloying with Gd from the magnetization data assuming that the Gd sites retain their full magnetic moment [75]. The moment on the Co-sites vanishes at around 80 atomic % Gd. The dependence of magnetic moment on the Co sites with composition suggests that besides the model described above, one could also argue that the observed decrease in TSP is due to a decrease in Co moment. The composition where the Co moment vanishes (and thus where the electrons tunneling from Co sites are unpolarized) corresponds to the composition where the TSP changes sign again. However, it is not possible to predict how the spin polarization will vary with the average magnetic moment on the Co atoms. Which explanation is more valid in this case cannot be fully answered.

Besides Co-Gd we also measured the TSP of various Co-Tb and Fe-Tb alloys (see table 3.1). Negative and positive TSP is also seen for some of those materials. Co-Tb and Fe-Tb are compensated at about 14 atomic % Tb. This is a lower RE fraction as compared to Gd reflecting the higher magnetic moment on the Tb atoms. For Co-Tb and Fe-Tb alloys the situation is complicated further as the Fe as well as Tb subnetwork spins are fanned out and not collinear. However, the same explanation for the sign reversal also holds for Tb based alloys.

The preceding experimental results on the tunneling spin polarization of Co-Gd
alloys show that the magnitude of the spin polarization depends sensitively on the tunneling matrix elements for tunneling from different elements. Even in the case of a vanishing net moment in these ferrimagnetic alloys sizable spin polarization is still observed. This reinforces the view that a spin polarized tunneling current can be created from a material that does not possess an overall spin imbalance. The results suggest that it should be possible to find materials with high polarization which have no net moment (e.g. an antiferromagnet). A prerequisite for such a material is that the electrons tunneling from different sites and sublattices (or sub-networks) have different tunneling probabilities and/or different spin polarization.

### 3.4 MTJs with RE-TM alloy electrodes

As described in the previous chapter, the tunneling spin polarization of Co-Gd alloys has been measured to be negative for a wide composition range. This TSP, measured using superconducting tunneling spectroscopy, can only be determined at low temperatures (<0.4 K, well below the critical temperature of the superconductor, which is Al₉₆Si₄ in our case). Superconductors with a higher critical temperature cannot be used because the spin orbit scattering (which is proportional to Z⁴) will lead to spin mixing in the SC [30].
In order to determine the spin polarization of Co-Gd alloys at higher temperatures one can use MTJs instead of FIS structures (see figure 3.12 for a schematic illustration). Here one does not use a SC counter electrode but rather a conventional ferromagnetic electrode (i.e. Co or Fe). Knowing the spin polarization of the counter electrode and measuring the TMR allows extraction of the polarization of the barrier/Co-Gd interface using Julliere’s formula (equation 2.2). As discussed before the TMR values calculated using the polarization of the electrodes measured with STS are usually an upper bound for the TMR measured at low temperature and zero bias. This is because for the TMR measurements the antiparallel alignment of the magnetizations is likely to be imperfect while the STS measurement is performed in a 2T applied field which very well orients the magnetic moments even at the interface. Nonetheless, the model can be used to qualitatively interpret data for TMR vs temperature in MTJs with Co-Gd alloys. A Co_{70}Fe_{30} counter electrode is used which is positively polarized as measured with STS. From equation 2.2 it is clear that a negative polarization of one electrode leads to negative TMR. Thus the sign of the TMR in a CoFe/barrier/Co-Gd MTJ directly gives the sign of the spin polarization of the barrier/Co-Gd interface at elevated temperatures.

In an MTJ built from electrodes one with positive and one with negative TSP the antiparallel state will have a a lower resistance than the parallel state. To be able to compare the TMR values of these structures with structures where the electrodes are either both positively or both negatively polarized one introduces a corresponding TMR defined as
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\[ TMR_{\text{neg}} = \frac{R_{AP} - R_P}{R_{AP}} = \frac{2P_1P_2}{1 + P_1P_2} \]  

(3.2)

where the denominator represents the low resistance state. This definition will be used in this thesis whenever either \( P_1 \) or \( P_2 \) (but not both) are negative.

We have fabricated and measured the TMR in MTJ structures of the following kind:

100Å Ta | 250Å Ir\(_{78}\)Mn\(_{22}\) | 35Å Co\(_{70}\)Fe\(_{30}\) | 23Å MgO | xÅ Co-Gd | 100Å Ta

Although the FIS samples with MgO and Co-Gd showed the highest TMR in the inverted structure here we use Co-Gd in the top electrode. In order to access a state with well defined antiparallel orientation of the electrodes one needs to be able to effectively exchange bias one of the electrodes. The exchange biasing has been found to be most effective when the lower ferromagnetic electrode is exchange biased. This also ensures proper growth of the MgO barrier. Exchange biasing Co-Gd was attempted but no significant exchange bias was observed. For the top electrodes, three different Co-Gd compositions were used: Co\(_{91}\)Gd\(_9\), Co\(_{74}\)Gd\(_{26}\), and Co\(_{40}\)Gd\(_{60}\). The thickness of the Co-Gd layer was varied in the case of Co\(_{74}\)Gd\(_{26}\) from 25Å to 500Å. For the other compositions the Co-Gd layer thickness was kept fixed at 300Å. The compositions correspond to the case where the TSP was measured to be positive (Co\(_{91}\)Gd\(_9\)) or negative (Co\(_{74}\)Gd\(_{26}\) and Co\(_{40}\)Gd\(_{60}\)). Due to the fact that the Gd and Co subnetworks have different temperature dependencies one expects to see a crossover from Gd dominated to Co dominated overall magnetization in Co\(_{74}\)Gd\(_{26}\) with increasing temperature [75, 67]. The compensation temperature depends very sensitively on the actual composition of the film. Co\(_{74}\)Gd\(_{26}\) was chosen as the compensation temperature is expected to be lower than room temperature and thus accessible for our standard magneto-transport measurement (which ranges from 4K to 330K). For Co\(_{91}\)Gd\(_9\) the Co network dominates over the whole temperature range while for Co\(_{40}\)Gd\(_{60}\) the Gd dominates up to the Curie temperature, which is well below room temperature for this compo-
3.4 MTJs with RE-TM alloy electrodes

Figure 3.13: TMR versus temperature for an MTJ with a Co$_{70}$Fe$_{30}$ electrode and a 300 Å thick Co$_{91}$Gd$_9$ counter electrode (upper panel). The lower panel shows the saturation magnetization of the Co$_{91}$Gd$_9$ layer versus temperature.

The TMR for the sample with a 300 Å thick Co$_{91}$Gd$_9$ top electrode is shown in the upper panel of figure 3.13. It is positive for temperatures up to 330 K. The decrease of the TMR with temperature is typical for MTJs and is believed to be due to inelastic scattering processes due to the excitation of spin waves [9, 88, 89]. In the lower panel the temperature dependent saturation magnetization of free and capping layer is shown. It measured with a SQUID magnetometer by separately measuring the saturation magnetization of the full stack and the bottom stack and subtracting these signals. Both bottom and full stack are on shadow masked
areas of size 2mm x 6mm that were deposited on the same wafer as the tunnel junctions. The saturation magnetization was measured in an applied field of 0.5 Tesla. The magnetization increases with temperature, reflecting the stronger temperature dependence of the Gd subnetwork as compared to the Co subnetwork. For this Co-Gd composition the Curie temperature is well above room temperature and not accessible with our SQUID magnetometer.

For Co$_{40}$Gd$_{60}$ the results are very different (see figure 3.14). Here the TMR is negative and vanishes around 200 K. This is the Curie temperature of the Co-Gd alloy as can be seen from the magnetization that levels off at this temperature.
The reason for the negative TMR is the negative TSP for the MgO/Co-Gd interface. As the Gd moment dominates over the whole temperature range we do not see positive TMR at all. The Curie temperature is reduced even below the $T_c$ of pure Gd ($\sim 300$ K) due to the fact that the Co-Gd exchange is much weaker than both Co-Co and Gd-Gd exchange [75].

By contrast MTJs with Co$_{74}$Gd$_{26}$ electrodes show positive and negative TMR depending on temperature (see figure 3.15). The sample shown here has a 50 Å thick top electrode. The transport measurements indicate a compensation temperature around 150 K. Below this temperature the TMR is positive and above it negative. The explanation is the same as already given in chapter 3.3: at the
Figure 3.16: TMR loops for the sample of figure 3.15 at various temperatures. The loops in panel a to e show the free electrode switching only. Panel f shows the complete TMR loop. The measurement temperature is indicated in the panels.

compensation point the relative orientation of the Co and Gd subnetworks reverses with respect to the applied field. The compensation point can also be inferred from the minimum in the magnetization in the bottom panel of figure 3.15. The compensation point determined from both the transport and magnetization measurement is the same (∼150 K). Typical TMR loops for various temperatures are shown in figure 3.16. Panel a and f show minor and major loops at 10 K. For simplicity, only the minor loops are shown for the other temperatures (panels b to e). Note how the coercivity increases as the temperature approaches the compensation temperature.

Changing the thickness of the film actually changes its compensation temperature. Figure 3.17 shows a plot of the compensation temperature versus Co-Gd film thickness. $T_{\text{comp}}$ increases with thickness and saturates at about 400 K for films thicker than >300 Å (for the films which have a compensation temperature above the accessible temperature range of the measurement system the magnetization
3.4 MTJs with RE-TM alloy electrodes

Figure 3.17: Compensation temperature ($T_{comp}$) for MTJs with a Co$_{70}$Fe$_{30}$ electrode and a Co$_{74}$Gd$_{26}$ counter electrode versus the thickness of the counter electrode which is varied from 25 to 500 Å. The compensation temperature is inferred from the sign reversal in TMR and minimum in the magnetization versus temperature data.

data was extrapolated to zero in order to extract $T_{comp}$). One possible explanation is that the target composition changes with during sputtering. However, there are no signs of a change in composition from the calibration films: RBS analysis indicates that these 1000 Å thick films have the same composition at all depths within the experimental uncertainty (±1 atomic %). Another possible explanation is that the Gd at the interface with the MgO gets partially oxidized, thus being driven magnetically inactive. The layer would then behave as a double layer comprised of an interface layer with reduced Gd moment and a layer of Co-Gd of the desired composition. Thus changing the thickness of the film would change the relative importance of the interface layer thereby changing the overall Co/Gd ratio and possibly increasing the compensation temperature with thickness.

Interestingly, the TMR at 10 K also increases with Co-Gd film thickness (see figure 3.18). This is an unexpected behavior as the TMR is believed to be very sensitive to the barrier/electrode interface [90, 91]. Thus, perhaps no more than 20 Å
Figure 3.18: TMR for MTJs with a $\text{Co}_{70}\text{Fe}_{30}$ electrode and a $\text{Co}_{74}\text{Gd}_{26}$ counter electrode whose thickness is varied from 25 to 500 Å. The TMR is measured at 10 K and 10 mV bias voltage.

of the top electrode closest to the barrier should largely determine the tunneling spin polarization. However, the results show that even an increase in Co-Gd thickness from 300 Å to 500 Å increases the TMR significantly. The reason for this is not entirely clear but maybe related to the alignment the interface spins. As already shown, for compositions around 25 atomic % Gd the TSP increases with increasing Gd content. This has to do with the fact that close to the compensation point the coercivity diverges and small changes in composition at the interface can produce regions where moments are compensated and which cannot be properly aligned in a field. Therefore increasing the relative Gd content will reduce coercivity and allow a more complete antiparallel alignment of the magnetizations of the electrodes.

The temperature dependence of TMR shown above for MTJs using Co-Gd electrodes shows some striking and unique features. At room temperature negative as well as positive TMR can be observed, depending on the composition. The magnetization and coercivity of the free layer (Co-Gd layer) can be tuned over a wide range. Obviously this can be achieved by changing the composition or by adding
other elements to the alloy (e.g. adding Tb increases the coercivity). While these are fascinating properties that not yet observed in other MTJ systems, there are some disadvantages which would likely prevent the use of these materials in applications such as MRAM: these drawbacks include especially their poor thermal stability and low room temperature TMR values. The maximum negative TMR obtained at low temperatures in the above tunnel junctions is around -15%. At room temperature only a few % can be realized. These values are low compared to conventional MTJs with two Co-Fe electrodes and MgO or Al₂O₃ barriers. Using MgO barriers TMR values of up to 220% at room temperature can be achieved [92]. For a complete discussion of these results see chapter 4. Even for Al₂O₃ barriers which show much lower TMR values one still observes values well above 40% at room temperature [8]. TMR values up to 70% have been reported using CoFeB electrodes [93]. For most of these materials the TMR typically increases upon cooling from 300 K to 10 K by about 50%. These arguments illustrate the need for a method to increase both TMR values and thermal stability of MTJs using RE-TM alloys.

### 3.5 MTJs with Co-Fe interlayers

#### 3.5.1 TMR and coercivity

To address the above drawbacks we have prepared MTJs with a thin Co-Fe layer between the barrier and the Co-Gd electrode (see figure 3.19 for a cartoon of the basic structure). The concept here is that because of the interface sensitivity of the tunneling process [90, 91] a highly spin polarized thin layer between the barrier and the Co-Gd will create a highly spin polarized tunneling current. If, as expected this interlayer is strongly exchange coupled to the Co-Gd electrode one should still be able to see negative TMR. The same idea has been used by Nishimura et al. to create high TMR in MTJs with perpendicular magnetization [94]. The material of choice for this interlayer is Co₇₀Fe₃₀ as it shows the highest spin polarization (~53%) of the transition metals alloys [41, 50]. The MTJ structure used is similar to the one already described in chapter 3.3:
Here $x$ and $y$ denote the thickness of the interlayer and RE-TM layer, respectively. For the RE-TM layer we used Co-Fe-Gd instead of Co-Gd. The main reason in using Co-Fe-Gd is that these targets are less brittle than Co-Gd targets. Although adding Fe changes some properties of the material (most noticeably the anisotropy; see chapter 3.7) the basic idea of the experiment is not altered as Co-Fe-Gd has the same antiparallel orientation of its subnetwork magnetizations as Co-Gd \cite{70, 75, 95, 96}. The Fe-Gd exchange is antiparallel while the Co-Fe exchange is positive so the magnetization of Co-Fe-Gd alloys behaves similarly to Co-Gd.

The bottom panel of figure 3.20 shows the TMR for MTJs of the above structure where the $Co_{70}Fe_{30}$ interlayer thickness is varied from 0 Å to 75 Å. The Co-Fe-Gd layer, whose thickness of 500 Å is not varied, has the nominal composition $Co_{35}Fe_{35}Gd_{30}$ which has a compensation temperature above RT. For zero interlayer thickness the TMR is about -6% similar to what has been observed with Co-Gd of comparable Gd composition (see chapter 3.4). Increasing the interlayer thickness increases the negative TMR until it saturates at around -45% for an interlayer thickness $\geq$15 Å. The TMR here is measured using major loops on the junction of the wafer that gave the highest TMR. The absolute value is insensitive to thickness for thicker interlayers until a sudden jump to a positive 35% for a 75 Å thick $Co_{70}Fe_{30}$ layer. Apparently, for an interlayer thicker than 15 Å the polarization
3.5 MTJs with Co-Fe interlayers

Figure 3.20: Free layer coercivity and TMR versus CoFe interlayer thickness for MTJs with a CoFe interlayer between barrier and $\text{Co}_{35}\text{Fe}_{35}\text{Gd}_{30}$ free layer of the tunneling current is completely dominated by tunneling from the interface layer.

![Graph showing free layer coercivity and TMR versus CoFe interlayer thickness](image)

The coercivity of the free layer is shown in the upper panel of figure 3.20. Here the coercivity of the free layer is measured from the hysteresis of the TMR versus field loops. It increases from 5 Oe to about 21 Oe with increasing interlayer thickness. Although the Co-Fe interlayer polarization is solely responsible for the high TMR one can see that the coercivity, measured form the minor loops, is determined not only by the interlayer but by the whole free layer stack ($\text{Co-Fe} + \text{Co-Fe-Gd}$). Due to the strong coupling between the layers the interlayer cannot switch independently. Thus, the coercivity is determined by the relative fraction of RE to
TM in the whole free layer. As the interlayer thickness is increased the relative proportion of Gd is decreased. The composition is moved closer to the compensation point and thus the coercivity increases [97]. For a thick enough interlayer the TM subnetwork dominates and the TMR becomes positive (as demonstrated in figure 3.20 where the TMR is positive for 75 Å of Co-Fe). Figure 3.20 shows the beauty of the structure used in these films: while the TMR maintains a high value the coercivity varies over a wide range. In addition to the coercivity, the magnetization of the whole free layer can be varied, thus allowing the engineering of the properties of the free layer for particular applications.

Figure 3.21 shows the TMR and free layer coercivity for samples where the interlayer thickness is fixed at 15 Å and the Co-Fe-Gd layer thickness is varied.
from 50 to 1000 Å. Here the compensation point lies between 50 and 100 Å at room temperature. The interpretation of the results relies on the fact that the coercivity and sign of TMR are dependent mainly on the relative proportion of RE to TM in the bilayer structure. This only holds to first order as the relative amount of Co to Fe will affect both the coercivity and the compensation temperature (which determines the sign of the TMR).

3.5.2 Thermal stability

Besides the low TMR in Co-Fe/MgO/Co-Gd structures their poor thermal stability is a major concern. For all the structures considered with Co-Gd and Co-Fe-Gd considered here thermal annealing leads to a dramatic drop in resistance and TMR. By contrast, MTJs using Co-Fe electrodes and MgO barriers are highly thermally stable to about 400°C (see chapter 4). Upon annealing the TMR and resistance typically increases up to a critical temperature at which the junction breaks down with loss of both resistance and TMR. While the insertion of a Co-Fe interlayer between the tunnel barrier and RE-TM electrode greatly increases the TMR it also positively affects the thermal stability.

Figure 3.22 shows TMR and resistance versus annealing temperature for MTJs with Co-Fe/Co-Fe-Gd top electrodes. Both 15 Å and 30 Å Co-Fe interlayer thicknesses were measured. A first annealing step is carried out in a batch anneal system in vacuum (base pressure $< 10^{-7}$ Torr) at 260°C in a magnetic field of 1 T in the plane of the film. Afterwards wafers are annealed one at a time in an automated single wafer annealing and measurement system. The sample is annealed to the desired temperature in vacuum (base pressure $< 10^{-7}$ Torr) and an applied in plane field of 0.4 T. After each anneal step the sample is then cooled down to RT where resistance and TMR are measured without breaking vacuum. This is performed automatically under computer control which allows for a thorough assessment of the behavior of the samples upon thermal annealing.

The MTJ 15 Å thick interlayer is stable to about 300°C. The TMR increases from $\sim -40\%$ to $\sim -75\%$ before the junction breaks down. The sample with 30 Å thick Co-Fe interlayer is slightly more stable (to about 310°C) and has higher
Figure 3.22: Dependence of resistance and TMR on annealing temperature for MTJs with 15Å (left panel) and 30Å (right panel) thick CoFe interlayers

TMR ($\sim -90\%$). The most likely reason why the interlayer improves the thermal stability of these junctions so much is that it prevents the RE atoms from reacting with the oxygen in the barrier. Doubling the thickness of the interlayer does increase the breakdown temperature only slightly. However, optimizing the growth of the barrier and choice of interlayer material is likely to improve the thermal stability.

### 3.5.3 Exchange coupling

Inserting a thin Co-Fe interlayer between the tunnel barrier and a RE-TM electrode significantly increases the absolute value of TMR and thermal stability of
these MTJs. This is possible because the Co-Fe interlayer is strongly exchange coupled to the Co-Fe-Gd layer (antiparallel to the Gd magnetic moment and parallel to the Co and Fe magnetic moments) – thus in sufficiently high fields the magnetic moment of the interlayer will be oriented opposite to the field. At still higher fields, however, the Zeeman energy will become larger than the exchange energy between the interface and the CoFeGd layer and the interlayer moment will also become aligned to the field. The reversal of the magnetization of the interlayer can be observed as a transition from a high to a low resistance state.

Figure 3.23: TMR loops for MTJs with 50 Å (left panel) and 25 Å (right panel) thick CoFe interlayer

Figure 3.23 shows the TMR versus field loops for two samples with different interlayer thicknesses where the field is increased to the maximum value available in the measurement apparatus (4000 Oe). While the exchange energy is constant with interlayer thickness $t$, the magnetostatic energy is proportional to $t$. Thus the field necessary to decouple the bi-layer is inversely proportional to $t$. While the samples with 25 Å thick interlayer show no decoupling of the layers up to 4000 Oe the sample with 50 Å thick interlayer already shows a decoupling at low field. The
interface energy per unit area $\Delta E$ can be calculated from

$$\Delta E = M_{FM} t_{FM} H_E$$  \hspace{1cm} (3.3)

where $M_{FM}$ is the interlayer saturation magnetization, $t_{FM}$ is the thickness of the interlayer and $H_E$ is the magnitude of the exchange field. Thus, $\Delta E$ is calculated to be

$$\Delta E = 1.5 \text{ erg/cm}^2$$

The interface energy is stronger compared to the exchange bias coupling at the IrMn/CoFe interface ($\Delta E = 0.19 \text{ erg/cm}^2$ [7]). For this reason compensated RE-TM films have been used to exchange bias FM films [98, 99].

In the preceding chapters it has been shown that Co-Gd alloys of certain compositions can show negative spin polarization. In MTJs negative TMR has been observed, even at room temperature. Using a thin CoFe interface interlayer remarkably high TMR values of greater than $-70\%$ were found after annealing. The thermal stability is also greatly improved and the interlayer has been shown to be well coupled to the Co-Gd layer. With these prerequisites being fulfilled one can think about using the negative RE-TM alloys to create devices with novel properties.

### 3.6 Double Tunnel Junctions

Double tunnel junctions are, as the name suggests, structures with three electrodes and two barriers (see figure 3.24 for a schematic diagram). Here the three electrodes are all magnetic. The dimensions of the middle electrode can critically influence the transport properties of the device. For thick enough middle electrodes a double tunnel junction can be viewed as two normal junctions is series but thin middle electrodes can lead to resonant tunneling effects or Coulomb blockade of current though the device. While in the DTJs discussed here Coulomb blockade does not play a role some of the characteristics for this regime shall nevertheless be discussed for completion.
Figure 3.24: Schematic diagram of a double tunnel junction. Two tunnel barriers (in grey color) separate the electrodes and form two single tunnel junctions (STJ) in series. The left and middle cartoons show side and top view, respectively. The right cartoon shows the top view of a single junction. The top electrode is drawn transparent and the middle electrode (orange square) can be seen.

In the Coulomb blockade regime the charging energy of the middle electrode is comparable to the applied voltage. Thus, electrons tunnel onto the middle electrode in discrete steps, leading to the so called Coulomb staircase in the IV curves. Coulomb blockade can only be observed if the thermal energy is lower than the charging energy of the middle electrode. There are two distinct tunneling processes by which the electrons can tunnel through the structure: sequential tunneling and cotunneling. In sequential tunneling the electrons tunnel through both barriers in an uncorrelated fashion. This is not the case for cotunneling where for each electron that tunnels onto the middle electrode another one simultaneously leaves it, so that the Coulomb energy is not increased. Cotunneling can be observed in the Coulomb blockade regime as sequential tunneling is strongly suppressed in this case. Theoretical calculations for magnetic double tunnel junctions in the Coulomb blockade regime predict an enhanced TMR due to cotunneling in these structures [100, 101], which has been verified experimentally [102, 103, 104, 105, 106]. Note that these effects can only be observed at very low temperatures which depend on the charging energy of the middle electrode.

If the middle electrode is reduced in thickness even further the tunneling process can be dominated by tunneling through localized states in the insulating barrier. Calculations show that the TMR can be enhanced in this case or even in-
verted [107, 108, 109, 110, 111] and experiments have partly verified those findings [112, 113].

If the middle electrode is thick enough then neither Coulomb blockade nor resonant tunneling will play a role and the tunneling process will be largely dominated by sequential tunneling. These structures can be thought of as two tunnel junctions connected in series. When the resistance and TMR of both single junctions is the same, the TMR of the DTJ is the same as that of the single junction. If the resistances are different then the overall TMR is lower than the higher TMR of the single junctions (no enhancement of TMR is expected). DTJs have attracted some interest as they are predicted to have a different voltage dependence as compared to STJs. The TMR has been found experimentally to decrease monotonically with applied bias. In the literature results for the bias dependence of the TMR are usually discussed in terms of $V_{50}$, the voltage at which the TMR is half of the zero bias TMR. Usually $V_{50}$ is lower than $\sim 0.5$ Volt. In a DTJ the voltage drop across one junction is half of the overall applied voltage. As the TMR is typically higher at low bias the TMR of the overall structure is higher at the same bias as compared to a STJ. Also, $V_{50}$ should be significantly increased [114, 103]. This may be useful for applications even though the DTJ has a more complicated structure. Another advantage is that the voltage across each junction can be much lower relative to the breakdown voltage, so the lifetime of the device is likely to be significantly increased.

Figure 3.24 shows a cartoon of a shadow masked double tunnel junction structure. The middle electrode is patterned as the small square. The bottom and top electrodes are fabricated in a cross stripe pattern but much wider than for a STJ. The active area of the junction here corresponds to the area of the middle electrode. Although there will be a tunneling current directly from the bottom to the top electrode in the area outside the middle electrode it is suppressed to a high degree as the tunnel barrier is double the thickness as compared to tunneling through the middle electrode (the tunneling current drops exponentially with increasing barrier thickness). However, in this configuration the middle electrode
Figure 3.25: TMR versus applied field at room temperature for a CoFe/MgO/CoFe/MgO/CoFe double tunnel junction with comparable top and bottom MgO barrier thicknesses. Panel a shows the full loop while the panel b shows only the low field part of the curve (switching of top and middle layer).

Both bottom and top Co$_{70}$Fe$_{30}$ layers are exchanged biased using two Ir$_{22}$Mn$_{78}$ layers. The exchange bias field is much smaller for the top electrode as compared to the bottom electrode but good enough to allow separation of the switching of top and middle (free) layer. The TaN/Ru layer on top serves as a capping layer. Different shadow masks that gave rise to different sizes of the active area of the DTJs were used. Some of them resulted in an active area much larger as compared to that of typical shadow masked single MTJs and therefore the barrier thickness cannot be biased.

Figure 3.25 shows the TMR loops versus field for a double tunnel junction with the following structure:

200Å TaN | 75Å Ta | 250Å Ir$_{78}$Mn$_{22}$ | 40Å Co$_{70}$Fe$_{30}$ | 40Å MgO | 30Å Co$_{70}$Fe$_{30}$ | 39Å MgO | 80Å Co$_{70}$Fe$_{30}$ | 150Å Ir$_{22}$Mn$_{78}$ | 75Å TaN | 75Å Ru
has to be increased for those DTJs, in order to achieve a junction resistance of around 1 kΩ. The TMR loops shown were taken after a thermal anneal at 260 °C for 90 min. The maximum TMR is around 90%. Note that three resistance states can be now observed. The resistance is highest when both STJs are in the antiparallel magnetization configuration and an intermediate resistance is achieved when the top STJ is in the low resistance state (parallel configuration) and the bottom STJ is in the high resistance state (antiparallel configuration). The magnitude of this intermediate TMR now depends on both the resistances and TMR of both STJs. For example, increasing the resistance of the top STJ while keeping the TMR constant would result in a lower intermediate TMR value.

This behavior is illustrated in figure 3.26 which shows MR loops for similar DTJs but for which the thickness of the top barrier is varied from 28 Å to 34 Å. Here, the overall TMR decreases with increasing barrier thickness. A relative change of top and bottom barrier resistance should not decrease the overall TMR. Hence the decrease in TMR indicates that the TMR of the top STJ is decreased, most likely due to an increased amount of defects with increase in barrier thickness.

The above TMR loops demonstrate that double tunnel junctions with high TMR and comparable resistance for top and bottom electrode can be reliably prepared. Using RE-TM alloys we can fabricate DTJs that show negative TMR. Figure 3.27 shows a double tunnel junction with Co_{30}Fe_{30}Gd_{40} as the middle electrode. Thin Co_{70}Fe_{30} interlayers are inserted between the Co-Fe-Gd layer and the tunnel barriers to increase TMR and thermal stability. Similar to the above DTJs both the bottom and top electrode are exchange biased and the middle electrode serves as a free layer. The structure is

\[
\begin{align*}
200Å \text{TaN} &\mid 75Å \text{Ta} \mid 250Å \text{Ir}_{78}\text{Mn}_{22} \mid 40Å \text{Co}_{70}\text{Fe}_{30} \mid 38Å \text{MgO} \mid 17.5Å \text{Co}_{70}\text{Fe}_{30} \mid \\
300Å \text{Co}_{30}\text{Fe}_{30}\text{Gd}_{40} \mid 17.5Å \text{Co}_{70}\text{Fe}_{30} \mid 38Å \text{MgO} \mid 100Å \text{Co}_{70}\text{Fe}_{30} \mid 150Å \text{Ir}_{22}\text{Mn}_{78} \mid \\
75Å \text{TaN} &\mid 75Å \text{Ru}
\end{align*}
\]

In the minor loop one can see that the middle and top electrode switching fields are well separated. The CoFeGd composition and thickness are chosen such that the electrode exhibits negative spin polarization at room temperature. The TMR loops are measured after a reset anneal at 260 °C. Reversal of the Co-Fe-Gd
layer magnetization results in both the bottom and top junction changing from a high to a low resistance state. The TMR is around $-50\%$ which is a lower than the TMR observed in comparable DTJs which use CoFe middle electrodes. The switching of the exchange biased top electrode can also be observed in the minor loop but the relative change in resistance is much lower than expected. If the resistance and TMR for both junctions were the same one would expect a resistance change upon switching of the top electrode that is half of the resistance change upon switching of the middle electrode. The observed resistance change is much lower indicating that either TMR or resistance of the top electrode is low. In fact it

Figure 3.26: TMR loops at room temperature for CoFe/MgO/CoFe/MgO/CoFe DTJs with varying top barrier thickness
can be expected that the TMR would be low for the top junction as the Co-Fe-Gd layer is amorphous and thus the upper Co-Fe interlayer as well as the MgO barrier and Co-Fe top electrode are not expected to grow as well textured as the bottom junction.

As discussed before it is desirable to reduce the magnetostatic fields in magnetic tunnel junctions used in MRAM elements. These arise from magnetic charges at the edges of magnetic layers and become larger the smaller the magnetic elements. It is not possible to simply reduce the volume of the magnetic material because the smaller the volume the more susceptible is the device to thermal fluctuations (i.e. super-paramagnetism). The same problem is encountered if materials with lower saturation magnetization are being used (such a material is e.g. Co-Pt [50]).
A more useful approach is to build a flux-closed device structure which can involve magnetic films with sufficient magnetic moment to be stable against thermal fluctuations. By balancing layers with opposite magnetic moments (and associated edge charges) stray fields can be minimized. A good example is the synthetic antiferromagnet used in recording heads and MRAM [6]

The DTJs described above are not flux closed and if one were to pin the magnetizations of the top and bottom electrodes in opposite directions to make them flux closed the TMR upon switching of the free layer (middle electrode) would be reduced (or even zero for STJ which have the same resistance and TMR). Using a material that is negatively spin polarized as the top or bottom electrode can give both low magnetostatic fields as well as high TMR. To demonstrate the feasibility of such a structure, DTJs using a negatively spin-polarized Co-Fe-Gd top electrode were prepared. The composition of the Co-Fe-Gd electrode is engineered such that its coercivity is higher than the coercivity of the middle electrode. This ensures that the hysteresis loops of middle and top electrode are well separated. Figure 3.28 shows the resulting MR loop. The middle electrode has the lowest coercivity followed by the top (Co-Fe-Gd) electrode.

Despite the difference in coercivities the magnetization reversal of the top and bottom electrodes are not very well separated. Also, the TMR does not switch abruptly with field with reversal of the Co-Fe-Gd layer. Indeed, saturation of the TMR is only achieved at relatively high fields (∼200 Oe). However, the data does show the basic elements of a flux closed DTJ using a negatively polarized top electrode. Upon reversal of the free layer (middle electrode) magnetization a TMR of around -33% can be achieved. This TMR value is much lower than the TMR observed in CoFe/MgO/CoFe/MgO/CoFe junctions, most likely due to edge effects, caused by electrodes which are not properly covered by the barrier material at the edges. It is likely that the use of materials which contain RE elements will lead to problems due to their high reactivity. However, the DTJ stack itself grows very well: Figure 3.29 shows a cross sectional TEM image of a flux closed double tunnel junction. Both the top and bottom barriers are very flat and the CoFe interlayer between the top barrier and the Co-Fe-Gd layer is continuous.
Figure 3.28: TMR versus field plots for a CoFe/MgO/CoFe/MgO/CoFe/CoFeGd double tunnel junction. The Co-Fe-Gd layer is not exchange biased but has a higher coercivity than the middle electrode (which serves as the free layer).

The above results demonstrate that high quality double tunnel junctions with separate switching of all three layers with field can be fabricated. Using RE-TM electrodes with negative spin polarization flux closed DTJs were prepared which showed a maximum TMR of -33%. These signal values can likely be much increased with improved sample preparation or exchange biasing of the RE-TM electrode.
3.7 Magnetic anisotropy in RE-TM alloys

One of the most useful properties of RE-TM alloys is that perpendicular magnetic anisotropy is found in a variety of RE-TM alloys such as Co-Gd, Fe-Gd, Co-Tb, and Fe-Tb. However, the magnitude of the anisotropy and even its sign (easy axis perpendicular to the plane or within the plane) changes considerably with the deposition technique and the deposition conditions for otherwise the same alloy composition [70]. For example, for both electron beam evaporation [115, 95, 75] and sputtering [116, 117], either in–plane or out–of–plane anisotropy was found in Co-Gd alloys. Besides the target composition, deposition parameters such as substrate bias, sputter gas pressure, power, applied magnetic fields during deposition, and oxygen incorporation [118] play important roles in determining the anisotropy magnitude and sign. Furthermore, thermal annealing and ion irradiation consid-

Figure 3.29: TEM image of a double tunnel junction with the following structure: IrMn/CoFe/MgO/CoFe/MgO/CoFe/CoFeGd. The image is courtesy of Phil Rice, IBM Almaden Research Center.
erably change the properties of the materials and usually decrease the magnitude of the anisotropy constant [119, 120, 121, 78].

Magnetic anisotropy can have diverse origins. Stress can induce anisotropy via the inverse magnetostriction effect. However experimental results indicate that stress does not play a major role in determining the anisotropy of Fe-Tb films [122]. Similarly, it was shown that shape anisotropy due to columnar microstructure and voids also does not play a dominant role [123]. Another mechanism for magnetic anisotropy is magneto-crystalline anisotropy due to a non-spherical electron density distribution (orbital moment) which is coupled to the spin moment. The interaction with the charge distribution of neighboring atoms (in the case of long range order) introduces a crystal field that leads to magneto-crystalline anisotropy. In the amorphous RE-TM alloys, where there is no long range order magneto-crystalline anisotropy can be ruled out as the dominant mechanism for magnetic anisotropy. However, short range order can introduce a local field which can give rise to anisotropy even in the absence of crystallinity. This short range order can be introduced via compositional directional short range ordering (CDSRO), basically an anisotropic environment of nearest neighbors for a given element. A special case of CDSRO is atom pair ordering [124, 125]. CDSRO has been experimentally confirmed in sputtered Fe-Tb films using EXAFS. Harris et al. showed that there is a significant difference in the relative number of Fe and Tb nearest neighbors in the plane compared to out of the plane [126]. This difference was predicted from the selective re-sputtering model. This model assumes that surface atoms can be selectively removed from different sites during the sputter deposition process due to differences in binding energies which depend on the local atomic environment of the surface atoms. This model can account for the experimentally found significant influence of substrate bias and sputter gas pressure on the magnitude of the anisotropy.

In the following, experiments to measure the magnetic anisotropy in Co-Gd and Co-Fe-Gd films will be presented. The purpose of these measurements was to check, in particular, the viability of using Co-Fe-Gd in MTJ structures for MRAM. MRAM MTJ elements which use the toggle mode of switching [127] require ma-
3.7 Magnetic anisotropy in RE-TM alloys

Materials with uniaxial anisotropy in the film plane with very low anisotropy fields ($H_k < 10$ Oe) and low coercivity. All the films were sputter deposited (as described in chapter 2.3) using DC magnetron sputtering from a Co-Gd or Co-Fe-Gd target respectively. The sputter power used was 80 W for all the films and the argon pressure during deposition was 3 mTorr. Permanent magnets close to the substrate position during deposition provide a $\sim 100$ Oe strong magnetic field in the film plane. This field is used to set the exchange bias direction of the pinned layer but is also present during deposition of the other layers.

Figure 3.30: Hysteresis loops for a 500 Å thick full film of Co$_{65}$Gd$_{35}$ at two different angles in the film plane.

As mentioned above, depending on deposition conditions, Co-Fe-Gd alloys can exhibit perpendicular anisotropy. However, all films fabricated here were found to
exhibit uniaxial anisotropy with the easy axis in the film plane. Figure 3.30 shows two representative magnetic hysteresis loops measured with a vibrating sample magnetometer on a 500 Å thick Co$_{65}$Gd$_{35}$ layer sandwiched between two 100 Å thick Ta layers (to prevent oxidization). The loops were measured in two orthogonal directions in the film plane. The loop along the easy direction shows a square hysteresis loop while the second loop, taken at an angle of 90° to the first one shows a hard magnetic behavior with an $H_k$ of about 15 Oe. The easy axis of magnetization was determined to be parallel to the field applied during deposition.

![Figure 3.31](image)

Figure 3.31: Saturation magnetization, coercivity, anisotropy constant, and anisotropy field for (Co-Fe)$_{1-x}$Gd$_x$ and Co$_{1-x}$Gd$_x$ films as a function of Gd concentration ($x$). The blue line indicates literature data for the saturation magnetization of Co-Gd alloys from [75]. The green lines are guides to the eye.

The same measurements were performed for a variety of Co-Gd and Co-Fe-Gd alloys with varying Gd concentrations. Figure 3.31 shows the saturation magnetization ($M_s$), coercivity ($H_c$), anisotropy field ($H_k$), and anisotropy constant ($K_u$)
3.7 Magnetic anisotropy in RE-TM alloys

for these films. The anisotropy constant was determined from $H_k$ and the magnetization $M_s$ using $K_u = 1/2H_kM_s$ [7]. The large error bars on the saturation magnetization data are due to the error in determining the film thickness and the error due to variations in measured magnetization for samples which are positioned differently with respect to the VSM pickup coils. The anisotropy field is strongly increased for Gd concentrations close to the compensation point. Indeed the dependence of $H_k$ on composition is similar to that of the coercivity which diverges at $T_{comp}$. Although at the compensation point $M_s$ vanishes and $H_k$ diverges, the product of both values ($K_u$) remains finite. In fact one finds that $K_u$ only varies slowly with composition. The anisotropy field and thus anisotropy constant are much higher for Co-Fe-Gd alloys as compared to Co-Gd alloys. These results are similar to the dependence of $K_u$ on Gd concentration in Co-Fe-Gd alloys with perpendicular anisotropy [95].

![Figure 3.32: Saturation magnetization, coercivity, anisotropy field, and anisotropy constant versus layer thickness for Co$_{44}$Fe$_{39}$Gd$_{17}$ and Co$_{58}$Gd$_{42}$ films](image)
The results in figure 3.31 correspond to measurements on \( \sim 500 \) Å thick RE–TM films. In useful MRAM MTJs, the layer thickness would need to be much lower to reduce the net magnetic moment and thus the stray fields. To investigate the influence of layer thickness we have measured the \( H_k \) and \( K_u \) for two different alloy compositions \((\text{Co}_{44}\text{Fe}_{38}\text{Gd}_{18} \text{ and Co}_{58}\text{Gd}_{42})\) for layer thicknesses ranging from 25 to 500 Å. The results are shown in figure 3.32. The anisotropy field and constant are much higher for Co-Fe-Gd as compared to Co-Gd samples for the whole thickness range and a pronounced decrease for thicknesses below 100 Å can be observed for both material systems. The decrease in anisotropy constant can be related to a decrease of the magnetization due to finite size effects \([128, 129]\) for films thinner than 100 Å. Above 100 Å thick films both \( H_k \) and \( K_u \) are relatively independent of thickness.

The dependence of the anisotropy on annealing was also investigated (see figure 3.33) because of its importance for MRAM, where the MTJs are subjected to high temperatures during processing. The films were annealed at various temperatures in a vacuum annealing furnace at \( < 10^{-7} \) Torr in an applied field of 1 T. Hard and easy axis loops were measured in a VSM. For some samples the angular remanence was also measured. Here the angle of the sample with respect to the magnet and pickup coils was varied in small increments up to a full revolution. At each angle, the film is saturated with an applied magnetic field of 1000 Oe, then the magnetic field is removed, and the remanent moment is measured. Samples with uniaxial anisotropy should show a characteristic pattern with a 180° period whereas samples with cubic anisotropy should show a period of 90°.

The magnetization of the samples is hardly affected by annealing up to 320° C. However, the anisotropy field shows a pronounced change upon annealing. For the thickest Co-Fe-Gd samples \( H_k \) increases slightly after annealing at 180° C but then stays basically constant upon further annealing. By contrast, for the Co-Gd samples \( H_k \) is decreased after each annealing step and after tempering at 260° the anisotropy field is reduced to below 2 Oe.
3.7 Magnetic anisotropy in RE-TM alloys

Figure 3.33: Anisotropy field ($H_k$) versus film thickness for Co$_{44}$Fe$_{39}$Gd$_{17}$ and Co$_{58}$Gd$_{42}$ films after annealing at various temperatures (as indicated in the plots)

However, after annealing at 300°C a distinctly different behavior is observed. The hard and easy axis can not longer be clearly distinguished and the film is nearly isotropic in the film plane. This is readily observed in angular remanence scans. Figure 3.34 compares the angular remanence for the 500 Å thick Co-Gd film after annealing at 260°C and 300°C, respectively. Clearly the shape of the curve changes dramatically and the uniaxial anisotropy is no longer present after annealing at 300°C. The angular remanence for the sample annealed to 300°C was measured using the vector coil setup of the VSM while the hysteresis loops and the angular remanence for the sample after annealing at 260°C were measured using a set of scalar coils. As the sample space for the vector coil setup is much smaller as compared to the scalar coil setup only a small piece of the sample could be measured which explains the much reduced magnetization values. These data provide clear evidence that the sample has crystallized. Indeed, the crystallization temperatures for Co$_{50}$Gd$_{50}$ is known to be around 300°C [130]). The angular remanence becomes characteristic of a polycrystalline sample with randomly oriented grains.
The fact that the anisotropy field decreases with increased annealing temperature is consistent with the mechanism in which the uniaxial anisotropy in these systems is derived from anisotropic short range order, as this order would likely be diminished with thermal treatments. The easy axis is oriented parallel with the field applied during deposition. Although the field is only 100 Oe it will orient the magnetization of the already deposited material. The exchange field is then likely to induce an anisotropic local chemical structure. To rigorously prove this point one would have to determine the local environment of Co or Gd atoms along different directions in the films (e.g. via EXAFS [126]).

The data show that for moderate anneals up to 260°C Gd rich Co-Gd alloys show very low coercivity (< 5 Oe) and anisotropy fields (< 5 Oe) making them interesting candidates for free layers in MRAM MTJs. However, the crystallization temperature is low and would likely need to be increased, e.g. with the addition of glass forming elements such as boron or zirconium. Whilst an increase of the crystallization temperature can also be achieved via the substitution of Co with Fe this results in a much higher anisotropy field.
3.8 Summary

In this chapter the tunneling spin polarization of rare earth–transition metal alloys, in particular Co–Gd and Co–Fe–Gd was investigated. We find that these alloys show both negative and positive TSP, depending on composition and temperature, a behavior that can be rationalized with the ferrimagnetic ordering of the RE and TM moments and high magnetization of the RE subnetwork. Interestingly, sizable TSP has been observed at the compensation point of the alloys where the net moment vanishes, illustrating that, in principle a perfect antiferromagnet can be expected to show a non–vanishing TSP, too. Using a CoFe interlayer a negative TSP of around $-50\%$ can be achieved at room temperature. The high spin polarization, as well as the tunable coercivity, amorphous structure and low uniaxial anisotropy of RE-TM alloys make them promising candidates for use in novel MTJ based devices, such as flux closed double tunnel junctions for MRAM memory cells.
Chapter 4

MgO tunnel barriers

Julliere’s model has been widely used in the past to explain the experimentally observed TMR and TSP values in MTJs and FIS structures (see chapter 2 for a complete discussion). However, the shortcomings and caveats of this model have been widely discussed in the literature [18, 131]. Because of the amorphous nature of the Al$_2$O$_3$ tunnel barrier, which has been almost exclusively used until recently, a theoretical treatment from first principles calculations has not yet been successful for this barrier material. By contrast, first principles calculations have been made for fully epitaxial structures using both vacuum barriers [132, 133, 134] and semiconductors such as Si, Ge, GaAs, and ZnSe [135, 136, 137, 138]. However, there are experimental difficulties in preparing high quality MTJs using these materials and the observed TMR values to date are low as compared to MTJs with Al$_2$O$_3$ barriers.

Recently, Butler [139] and Mathon [140] have calculated spin polarized transport in fully epitaxial Fe/MgO/Fe sandwiches. They find that the tunneling conductance depends strongly on the symmetry of the Bloch states in the electrodes and the evanescent states in the MgO barrier. In particular, Bloch states decay at different rates through the barrier layer depending on their symmetry and interfacial resonance states with particular in–plane momentum tunnel effectively through the barrier. Figure 4.1 shows the dependence of majority and minority conductance on momentum parallel to the barrier for various numbers of MgO layers. While the majority transmission, at least qualitatively, looks similar to the
Figure 4.1: Majority (left panel) and minority (right panel) conductance versus the crystal momentum in the film plane for a (100)Fe/MgO/Fe structure with 4, 8, and 12 layers of MgO (from [139]).

In the case of a free electron incident on a square barrier the minority conductance clearly does not. The conductance is strongly enhanced for values of $k_{∥}$ close to interfacial resonance states. Figure 4.2 shows the tunneling density of states for $k_{∥}=0$ for Fe(100)/8MgO/Fe(100). States with $\Delta_1$ symmetry, which are only present in the majority channel, decay much more slowly in the barrier than states with $\Delta_5$ and $\Delta_2'$ symmetry.

Both Butler [139] and Mathon [140] predicted a high TMR in excess of 1000% for Fe(100)/MgO(100)/Fe(100) tunnel junctions with thick enough MgO layers. Furthermore, an increase of TMR with barrier thickness was calculated since for thicker barriers the filtering effect of the different decay rates for states with different symmetries is enhanced.
Many experimental efforts were undertaken to verify the predictions of extraordinary high TMR in Fe/MgO/Fe. Bowen et al. fabricated Fe/MgO/FeCo(001) MTJs using a combination of sputtering and pulsed laser deposition (PLD) on GaAs(001) [141]. They observed a TMR value of only 27% at room temperature and 60% at 30 K. Wulfhekel et al. prepared Fe/MgO/Fe(001) junctions on single crystal Fe(001) substrates and Fe whiskers by MBE and PLD [142]. They claimed to prepare single crystalline and flat junctions but were not able to measure the TMR due to experimental limitations. In the same group the interface of MgO grown on Fe(001) single crystalline substrates was investigated via surface x-ray diffraction. An FeO interface layer between the Fe surface and the MgO layer was found [143, 144]. Following these results Butler et al. calculated
the effect of this FeO layer on electronic structure and tunnel magnetoresistance in Fe/FeO/MgO/Fe structures [145]. They find that the FeO layer significantly reduces the TMR due to a reduced conductance for parallel alignment of the magnetization of the electrodes. Despite these discouraging results Popova et al. prepared Fe/MgO/Fe/Co tunnel junctions on single crystal MgO(001) substrates using MBE obtaining a TMR of 17% at room temperature [146]. By increasing the tunnel barrier thickness to $\sim 25 \text{Å}$ the same group was able to obtain TMR values up to 67% at room temperature and $\sim 100\%$ at 80 K [147]. The MgO layer in these MTJs is deposited with electron–beam evaporation. Mitani et al. prepared Fe/MgO/Fe(001) junctions where the barrier was formed by plasma oxidization of Mg metal but only found a TMR of 20% at 77K [148]. Very recently Yuasa et al. reported a TMR of 88% at room temperature for fully epitaxial Fe/MgO/Fe(001) junctions prepared by MBE [149].

Kant et al. measured the spin polarization of Fe and Co with MgO barriers using STS. They found even lower TSP values for both Co and Fe electrodes ($\sim 30\%$) than for control junctions with Al$_2$O$_3$ barriers ($\sim 40\%$) [150].

Sofar, the observed TMR (and TSP) values are much lower than those predicted. Furthermore, the TMR values are lower than the highest TMR values reported using conventional amorphous Al$_2$O$_3$ barriers (with the exception of Yuasa’s results which, in any case, are only slightly higher). Possible reasons for such low TMR values might be FeO interface layers between MgO barriers and Fe electrodes or disorder in the MgO barrier. While calculations are carried out for perfectly epitaxial systems, in real junctions there will always be a degree of disorder present which might destroy the coherence of the wave functions. The influence of disorder has been theoretically treated with various approaches for magnetic multilayers [151] and MTJs [152, 153] but not yet for Fe/MgO/Fe sandwiches.

The low TMR values make it difficult to judge whether coherent transport plays an important role in Fe/MgO/Fe tunnel junctions. To verify the theoretical predictions one needs to prepare high quality junctions which show a higher TMR as compared to control samples with Al$_2$O$_3$, and which show a TMR that increases with barrier thickness.
To attempt to confirm the predictions of high TMR we have prepared tunnel junctions using MgO barriers and Fe or Co-Fe as electrode materials (chapter 4.1). The main focus of this work, however, was the preparation of FIS structures to measure the spin polarization of the FM/MgO interface. The dependence of TSP on thermal annealing (section 4.2), structure (section 4.4), FM material (section 4.4) as well as crystallographic orientation of the FM (section 4.4) was investigated.

## 4.1 MTJs with MgO barriers

Following the above motivation we fabricated MTJs with Fe and Co-Fe electrodes at ambient temperature using a combination of magnetron and ion beam sputtering. Typical resistance versus field curves are shown in figure 4.3. The lower ferromagnetic electrode is formed by first depositing an underlayer of 100 Å of TaN on an amorphous layer of SiO₂ formed on a Si(100) substrate. An antiferromagnetic layer of Ir₁₂₂Mn₇₈, which is used to exchange bias the lower FM layer is then deposited by ion beam sputtering, followed by the FM layer, which is formed from a bilayer of 8 Å Co₈₄Fe₁₆ and either 18 Å Fe (panels a and b) or 30 Å Co₇₀Fe₃₀ (c-f). The MgO layer is formed by reactive magnetron sputtering in an argon-oxygen mixture (3 mTorr). Growth conditions were optimized to give nearly stochiometric MgO. The upper ferromagnetic electrode is formed from a layer of Co₈₄Fe₁₆ with capping layers formed from TaN or Mg. These are the complete structures for the samples shown in figure 4.3:

(a) and (b) 100Å TaN | 250Å Ir₂₂Mn₇₈ | 8Å Co₈₄Fe₁₆ | 18Å Fe | 27Å MgO | 100Å Co₈₄Fe₁₆ | 100Å TaN

(c) and (d) 100Å TaN | 250Å Ir₂₂Mn₇₈ | 8Å Co₈₄Fe₁₆ | 30Å Co₇₀Fe₃₀ | 29Å MgO | -150Å Co₈₄Fe₁₆ | 100Å Mg

(e) and (f) 100Å TaN | 250Å Ir₂₂Mn₇₈ | 8Å Co₈₄Fe₁₆ | 30Å Co₇₀Fe₃₀ | 31Å MgO | -150Å Co₈₄Fe₁₆ | 100Å Mg
4.1 MTJs with MgO barriers

Figure 4.3: Room temperature TMR versus field plots for MTJs with MgO barriers and Fe and Co-Fe electrodes. For a complete sample description see text. Panels (a), (c), and (e) show major loops while panels (b), (d), and (f) show the corresponding minor loops. Results for different annealing temperatures are shown. The annealing temperatures are indicated in the plots. The sample in panels (a) and (b) has a higher exchange bias field as compared to the others due to a thinner bottom electrode.

Very large TMR values are found ranging from $\sim 120\%$ to more than $165\%$ at room temperature. These high TMR values are obtained after field annealing at high temperatures up to $380^\circ$C. Unannealed samples usually show TMR values of around $50\%$. Annealing at higher temperatures leads to loss of both resistance and TMR. The sample with the Fe electrode shows a much lower TMR as compared to the one with Co$_{70}$Fe$_{30}$ ($\sim 120\%$ as compared to $\sim 165\%$).
Figure 4.4 shows a TEM image of a MTJ structure similar to the one shown in panel (c) and (d) of figure 4.3. The image shows an excellent morphology with extremely smooth and flat layers. Both Co-Fe layers are bcc with a (100) texture while the MgO is cubic (NaCl structure) and also (100) textured. Although the samples are highly textured they are polycrystalline with a random orientation of the grains in the plane. Also, figure 4.4 (panel a and c) reveals a number of stacking faults along the (111) planes in the IrMn layer which propagate through the whole structure.

In MTJs where the resistance of the electrodes is similar to the resistance of the tunnel junctions themselves non-linear current distribution can lead to artificially enhanced TMR values [154, 155]. However, the results in figure 4.3 panels (c) to (f) illustrate that the high TMR values shown here are not artificially enhanced. Panels (e) and (f) show TMR values for a sample with a 2000 times higher junc-
4.1 MTJs with MgO barriers

tions resistance as compared to the resistance of the electrode. For this sample current crowding effects can be ruled out and the TMR after annealing at 360°C is comparable to the TMR of the sample shown in panels (c) and (d) which has a much lower resistance (only 6 times higher than electrode resistance).

Furthermore, the high TMR values were reproduced using the technique of current-in-plane tunneling (CIPT)\cite{156} on un-patterned films. The CIPT measurements confirm the results obtained with shadow-masked junctions and show even higher TMR (up to 220%) for structures with a lower RA product (200% TMR were obtained on a MTJ stack with RA~10^4 \Omega(\mu m)^2). However, no significant variation of TMR with MgO barrier thickness was found, contrary to theoretical predictions of rapidly increasing TMR with MgO thickness.

Figure 4.5 shows the temperature dependence of RA product in parallel and antiparallel configuration and the resulting TMR value for the two junctions with Co-Fe electrodes (the same junctions as shown in figure 4.3 panels (c)-(f)). For both samples the TMR increases to nearly 300% at 4K. The increase in TMR results mainly from an increase in resistance for the antiparallel alignment of the magnetization of the electrodes while the resistance for parallel alignment is hardly affected.

The above results are perhaps the first conclusive evidence for effects of coherent transport in epitaxial tunnel junctions. The observed TMR in CoFe/MgO/CoFe MTJs of 165% (up to 220% measured by CIPT) is well above the highest values measured for comparable CoFe/Al_2O_3/CoFe junctions. The results can likely be explained in the above discussed framework of coherence of wavefunctions through the epitaxial MgO barrier. It is found that the TMR increases dramatically with thermal annealing. Indeed, before annealing the TMR is no higher than for comparable MTJs with amorphous Al_2O_3 barriers. The thermal anneal treatments likely improve the epitaxy of the barrier. Although the effect of disorder is not discussed in the original theoretical work it is likely that disorder will decrease the TMR as it will decrease the coherence of the wave functions. In turn, improving the epitaxy
Figure 4.5: Temperature dependence of resistance (in parallel and antiparallel configuration) and resulting TMR for two junctions with Co-Fe electrodes (the same junctions as shown in figure 4.3 panels (c)-(f)).

(for example due to thermal annealing) will increase the TMR as observed.

The TMR for Co\textsubscript{70}Fe\textsubscript{30} based junctions was significantly higher than for Fe based MTJs (165\% as compared to 120\%). This is likely due to an improved interface structure, which has also been seen for Co\textsubscript{70}Fe\textsubscript{30} and Fe using Al\textsubscript{2}O\textsubscript{3} barriers. The addition of Co probably reduces the tendency to form a FeO interface layer which is calculated to decrease the observed TMR. Co-Fe alloys for up to \(\sim\)90\% Co are bcc and grow with a (100) texture on Ta/IrMn underlayers as determined from TEM images. Thus, it is likely that the theoretical framework that was developed for Fe/MgO/Fe still holds for a range of different bcc Fe alloys.
The experiments do not show a significant increase of TMR with MgO barrier thickness. This is probably due to the fact that for thicker barriers structural disorder is increased and thus the coherence of the wavefunctions through the barrier is lost so limiting the spin–filtering effect. However, more experiments are needed to confirm this point.

### 4.2 TSP of the Fe/MgO interface

The spin polarization of the FM/MgO interface was measured directly using superconducting tunneling spectroscopy. Although this technique allows one to investigate both the bottom and top interfaces separately, to maintain a highly epitaxial and textured FM/MgO layer it is necessary to grow these on appropriate underlayers. Thus, the inverted FIS structure was used with the superconductor (Al$_{96}$Si$_4$) forming the top electrode. As described earlier in chapter 2 the shadow mask set in this case is different from the mask set used to fabricate MTJs. The structure and underlayers, however, are very similar. Figure 4.6 shows the tunneling spin polarization for the following structure:

$$75\text{Å} \text{Ta} | 250\text{Å} \text{Ir}_{22}\text{Mn}_{78} | 8\text{Å} \text{Co}_{84}\text{Fe}_{16} | 18\text{Å} \text{Fe} | 24\text{Å} \text{MgO} | 59\text{Å} \text{Al}_{96}\text{Si}_4$$

After the samples were fabricated, the TSP was measured before any thermal treatments were carried out (this is the 25°C data point shown in the plot). The samples were then successively annealed at steadily increasing temperatures, for 20 min at each temperature. The TSP was measured after each annealing step. Figure 4.7 shows the conductance curves for the sample of fig 4.6 after several annealing steps. The increasing difference in height of the two peaks shown here in figure 4.7 at small bias voltage is a simple measure of the magnitude of the TSP.

The unannealed sample shows a TSP of 57.5% which is already much higher than previously measured for the Fe/Al$_2$O$_3$ interface (45% [41]). Upon annealing the TSP values increase almost linearly with anneal temperature to 75% after annealing at 380°C. A high temperature anneal at 400°C resulted in shorting of the junctions. The high TSP values appear to be consistent with the first principles calculations of Butler and Mathon although these calculations were limited
Figure 4.6: Tunneling spin polarization of the Fe/MgO interface versus annealing temperature. The structure is Ta/IrMn/CoFe/Fe/MgO/AlSi (see text).

to (100)Fe/MgO/Fe. The significant increase of TSP with annealing temperature suggests that the epitaxial quality of the MgO layer and the Fe/MgO interface structure are important. These are likely to be improved with thermal anneal treatments.
4.3 Influence of electrode material and structure on TSP

Figure 4.7: Conductance versus applied voltage curves after various annealing treatments for an Fe/MgO/AlSi i-FIS structure

just as for the Fe/MgO interface, the TSP is dramatically increased upon annealing from a modest value as deposited (52%) to 85% after annealing at 410°C. This value is about 10% higher as compared to the highest TSP measured for the Fe/MgO interface. After annealing at 420°C the samples were shorted. However, the CoFe based samples are more thermally stable than the Fe based ones which broke down after annealing at 400°C.

The theoretical treatment of Fe/MgO/Fe structures emphasizes that the matching of the wavefunctions in both electrodes plays an important role in determining
Figure 4.8: Tunneling spin polarization of the Co$_{70}$Fe$_{30}$/MgO interface versus annealing temperature. The structure is Ta/IrMn/CoFe/MgO/AlSi (see text)

the overall tunneling current. In the case of the AlSi layer however, it is unlikely that this plays a role, as the electronic structure of AlSi is very different from Fe and CoFe. However, the different decay rates in the barrier for electrons with different symmetries should still spin filter the tunneling electrons in Fe/MgO/AlSi structures. Following this argumentation one can reason that a lower bound for the TMR at low temperatures of a FM/MgO/FM MTJs can now be calculated using the experimentally observed TSP and Julliere’s formula. Assuming two similar interfaces a TSP of 80\% corresponds to 355\% TMR (this is calculated using equation 2.2). This value is slightly higher than the 300\% TMR which has been experimentally observed at low temperature (see figure 4.5) which may point to the fact that the electrons loose the coherence upon tunneling through a part of the barrier and no additional filtering in the counter electrode occurs.

A higher spin polarization and TMR for Co$_{70}$Fe$_{30}$ electrodes is measured as compared to Fe electrodes. This is either because of improved structural perfection for CoFe compared to Fe electrodes, for example due to a lesser oxidation of the top electrode, or because of a more fundamental reason such as a higher density
of states for s–like electrons ($\Delta_1$ states) as has been predicted for Co [157].

Figure 4.9: Resistance versus annealing temperature $Ta/IrMn/CoFe/MgO/AlSi$ i–FIS junction

The resistance of the STS samples is dramatically increased upon annealing. Figure 4.9 shows a plot of the junction resistance versus annealing temperature. After a final anneal at $410^\circ C$ the resistance is increased from that before annealing by a factor of $\sim 35$. This dramatic increase of resistance is not observed for MTJs, which perhaps suggests that it is caused by the superconducting layer although the MTJs usually break down at lower anneal temperatures. Thus a possibility is that defects in the MgO tunnel barrier (which most likely account for the low tunnel barrier height of $\sim 1\, eV$) are annealed out, so increasing the tunnel barrier height and the corresponding barrier resistance. Another possible explanation is that the effective barrier thickness increases due to an oxidization of the AlSi electrode (which, in this case would have to extract oxygen from the MgO barrier) or a more complex interface reaction involving the formation of Mg–silicate and –aluminate compounds at the interface of the AlSi to the MgO barrier.
The samples above were all grown in the inverted structure, that is with the SC on top, to be able to control the growth of the MgO barrier by selection of appropriate underlayers. However, the samples can also be grown with the SC on the bottom (normal structure). Figure 4.10 shows the TSP versus annealing temperature for samples with the following structure

\[
\begin{align*}
\text{Al}_{96}\text{Si}_{4} | \text{MgO} | \text{Co}_{70}\text{Fe}_{30} \\
\text{Co}_{70}\text{Fe}_{30} | \text{Al}_{2}\text{O}_{3} | \text{Al}_{96}\text{Si}_{4} \\
\text{Al}_{96}\text{Si}_{4} | \text{Al}_{2}\text{O}_{3} | \text{Co}_{70}\text{Fe}_{30}
\end{align*}
\]

The polarization before annealing is comparable to the samples in the inverted structure but upon annealing the TSP at first decreases slightly and then decreases dramatically for annealing at temperatures higher than 260°C. The reason for the low TSP could be due to an imperfect growth of the MgO barrier on the AlSi layer. The poor texture and disorder in the MgO layer is likely to destroy the coherence of the wavefunctions. Thus, it is not possible to conclude from these observations that the top interface of CoFe/MgO/CoFe junctions is weakly polarized, since in the MTJs the texture is preserved throughout the layers.
In addition the TSP of samples in the inverted and normal structures using Al$_2$O$_3$ barriers was investigated. The results are shown in figure 4.10 for which the samples have the following structures:

**Figure 4.10 (●)** 100Å Ta | 250Å Ir$_{22}$Mn$_{78}$ | 35Å Co$_{70}$Fe$_{30}$ | 16Å Al | plasmaoxidization | 60Å Al$_{96}$Si$_4$

**Figure 4.10 (♦)** x Å Al$_{96}$Si$_4$ | 14Å Al | plasmaoxidization | 200Å Co$_{70}$Fe$_{30}$ | 100Å Ta

The AlSi thickness for the samples in the normal FIS structure (x) was varied from 45 Å to 65 Å and the plasma oxidization time was varied from 180 s to 300 s. Multiple data points for specific annealing times in figure 4.10 correspond to different samples with different AlSi thicknesses or different plasma oxidization times. However, the measured TSP value is insensitive to a change in these parameters within the experimental uncertainty. For these samples the TSP decreases for annealing temperatures above 220°C and no enhanced TSP is observed. This result is somewhat striking as in MTJs thermal annealing leads to a significant increase in TMR. However, this increase might occur due to improved switching of the magnetization of the electrodes. As the STS measurements are performed at an applied 2 T poor switching does not influence the measurement. Given that the thermal anneal treatment dependence of the normal FIS structures with CoFe is the same for both MgO and Al$_2$O$_3$ barriers, we can conclude that the lack of electrical isolation pads (shown in figure 2.10), which also protect the edges of the AlSi electrode causes the low TSP values for samples with CoFe and MgO barriers in the n-FIS structure.

### 4.4 Influence of orientation on TSP

A Ta underlayer together with an IrMn exchange biasing layer causes the Fe or CoFe layers as well as the MgO layer to grow with a (100) orientation, as confirmed by TEM imaging. Here the IrMn layer is also (100) oriented. For this orientation of the electrodes and MgO the theoretical calculations predict a highly spin polarized tunneling current. No calculations have been performed for orientations of Fe or
CoFe other than (100) because the epitaxial relationship of bcc Fe (and bcc CoFe) and MgO is only known for the (100) orientation. Moreover, in this orientation the bcc Fe and simple cubic MgO lattices have an almost perfect lattice matching (their lattices are rotated by 45°). However, using STS the influence of the orientation of the films can be investigated experimentally. The orientation of the CoFe and MgO layers can be changed by growing them on appropriate underlayers. While Ti, Ta, TaN, and TaN/Ta bilayers lead to (100) oriented IrMn, CoFe and MgO, using Ta/Pt or Ti/Pd underlayers the IrMn is (111) textured, bcc CoFe is (110) oriented and the MgO grows (111) textured.

Figure 4.11: TEM images with low (upper panel) and high magnification (lower panel) for the following MTJ structure: 50ÅTa / 150ÅPt / 250ÅIrMn / 25ÅCoFe / 40ÅMgO / 100ÅCoFe / 100ÅTaN. The high magnification image reveals that CoFe grows (110) oriented on the (111)IrMn and the MgO layer has a (111) texture. The image is courtesy of Phil Rice, IBM Almaden Research Center.

Figure 4.11 shows a TEM image of an MTJ stack that has an underlayer of 50ÅTa/150ÅPt/250ÅIrMn. Although the top layer is obviously different from the FIS samples the image shows the growth relationship of CoFe and MgO on the (111) oriented IrMn. Note that the IrMn does not grow as flat in the (111)
4.4 Influence of orientation on TSP

orientation as in the (100) orientation (compare to figure 4.4), thus the CoFe layers and the MgO layers are also considerably rougher. There are significant amounts of grain boundaries in the IrMn layer that propagate through the entire stack. However, the high magnification image reveals that the CoFe grows (110) oriented and the MgO has a (111) texture.

The dependence of TSP on these different underlayers was investigated by measuring the TSP for the following structures:

**Figure 4.12:** *underlayer | 250Å Ir_{22}Mn_{78} | 35Å Co_{70}Fe_{30} | y MgO | 60Å Al_{96}Si_{4}*

with the following underlayers:

- 75 Å TaN | 50 Å Ta | 150 Å Pt
- 100 Å TaN | 75 Å Ta
- 75 Å Ti | 150 Å Pd
- 50 Å Ti

![Figure 4.12: TSP versus annealing temperature for CoFe/MgO stacks grown on various underlayers (as indicated in the graph)](image-url)
The results for the annealing temperature dependence of the TSP are plotted in figure 4.12. All samples are stable to 380 °C but most of them break down after anneal at 420 °C. There is some scatter in the results due to experimental uncertainties and a variation of TSP values for different junctions on the same wafer. However, the TSP values for all the samples increase almost linearly. The samples with Ti and Ti/Pd underlayers initially have a lower TSP as compared to the samples with Ta based underlayers. However, the TSP is similar for all the samples after annealing at 380 °C. The results reveal that both CoFe(100)/MgO(100) and CoFe(110)/MgO(111) show high TSP, although the roughness of the layers is considerably higher for the case of (111) oriented IrMn. These results are somewhat striking as the high TMR calculated in (100)Fe/(100)MgO/(100)Fe structures is believed to be due to features quite unique to the (100) orientation.

MTJs with (111) oriented MgO using a wide variety of underlayers were also prepared in addition to the FIS structures. In contrast to the STS results the (111) oriented samples usually show a much lower TMR as compared to the control samples that use (100) MgO barriers. This may be caused by an imperfect top interface due to roughness in the films. Using STS one cannot determine the TSP of the MgO/CoFe interface for different orientation, as the highly disordered AlSi does not allow proper epitaxial growth on top of it. More experiments will be needed to investigate the influence of different textures on the spin dependent transport in these films. To complement these experiments it would be useful to calculate the spin polarized transport for CoFe(110)/MgO(111)/CoFe(110) layers theoretically.

4.5 Summary

In this chapter high TMR (up to 220%) was demonstrated for MTJs with MgO barriers and the bcc ferromagnets Fe and Co$_{70}$Fe$_{30}$. Similarly a high TSP was found for Fe/MgO and Co$_{70}$Fe$_{30}$/MgO interfaces. Both TMR and TSP increase significantly upon annealing. The values measured are the highest ever measured for non half-metallic electrodes and are much higher than the TSP for interfaces of the CoFe and Fe to Al$_2$O$_3$. This demonstrates that a ferromagnetic material does
not have a unique spin polarization but rather depends on the ferromagnet/barrier combination. Similar conclusions have previously been inferred from changes in the sign of TMR for junctions containing SrTiO$_3$ barriers and Co and manganite ferromagnetic electrodes as a function of bias voltage [158].

The TMR and TSP values obtained are significantly higher than results published previously for MTJs with MgO barriers and validate theoretical calculations that predicted TMR values for these material combinations. However, the theoretically predicted values are still higher than the experimental values most probably due to disorder in the barrier and imperfect interfaces. It can be anticipated that improved sample fabrication will lead to even higher TSP and TMR values. Although the high TMR predicted by the calculations could be experimentally verified the samples did not show the predicted increase of TMR with barrier thickness. This behavior can be attributed to increased disorder for thicker barriers.

However, some experimental results remain to be fully understood. The TSP does not depend on whether the Co-Fe electrode is (100) or (110) oriented while in MTJs the orientation has a significant influence on the measured TMR. Furthermore, the influence of the superconducting layer on spin polarization of the tunneling current will have to be clarified. While experimentalists strive to prepare more perfect structures it would be helpful to be able to calculate tunneling currents for the case of a disordered system.

The above results are not only relevant from a scientific point of view but also of tremendous technological interest. The experiments demonstrate that MTJs with high TMR can be obtained using relatively simple and inexpensive sputtering techniques. Furthermore, complex magnetically engineered structures can readily be built by using exchange biasing and oscillatory interlayer coupling. It is thus likely that MTJs using MgO barriers will have a major impact on technologically relevant spintronic devices. For example, higher signal levels will accelerate the implementation of advanced MRAM architectures [159].
Chapter 5

Conclusions

The experiments performed in the framework of this thesis were aimed at deepening the understanding of spin polarized tunneling. The spin polarization of rare-earth transition metal alloys has been investigated – these alloys are one of very few material systems that show negative tunneling spin polarization. The dependence of TSP on composition can be understood in the framework of a simple model that takes into account tunneling from both TM and RE atoms considering their respective tunneling probabilities. The results show that sizable spin polarization can be observed in materials which have vanishing magnetization (as a result, non-vanishing TSP can be expected for antiferromagnetic materials). Materials with negative TSP can be used in tunnel junctions which show sizable negative TMR at room temperature. Moreover, these materials can be tailored to possess low magnetization, low coercive field and low anisotropy fields making them promising candidates for applications like flux closed double tunnel junctions for MRAM. The basic working principle of DTJs has been experimentally verified. However, more work will be needed to optimize the structure and the switching properties of the magnetization in these complicated multilayers.

Besides the importance of tunneling matrix elements it has been shown that coherent tunneling of electrons can be observed in highly textured Fe/MgO/Fe junctions deposited via magnetron sputtering. For these material systems a high TMR (>1000%) has been theoretically predicted. Although values this high could not be achieved the measured values (>200%) by far exceed the maximum TMR
values obtained with conventional $\text{Al}_2\text{O}_3$ barriers ($\sim 70\%$). Moreover, similarly high TMR values have been found for MTJs using Co-Fe electrodes with up to 86 atomic % of Co. The results demonstrate that the tunneling process is highly dependent on the band structure in both electrode and barrier. Not all of the theoretically predicted features could be observed though, illustrating the need for more measurements and more calculations. It is desirable to extend the first principle calculations to disordered material systems as well as improve the epitaxial quality of the samples, to allow a more direct comparison of theory and experiment.

The results discussed in this thesis have the potential to be relevant for device applications such as magnetic random access memory and spin injection into semiconductors. Magneto-electronic devices are successfully being used today in recording read heads and the commercial availability of MRAM seems imminent. Bold steps are being undertaken to use spin polarized currents for logic elements which might become a reality in the future.
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