Probing spin polarization: point contacts and tunnel junctions

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Probing spin polarization

Point contacts and tunnel junctions

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The cover is an artists impression of electrons and Cooper pairs near an interface.
Contents

1 General introduction ............................................ 1
  1.1 Magnetoresistive devices and applications ................. 1
  1.2 Spin polarization of an electric current .................. 4
  1.3 Outline of this thesis ....................................... 11

Part I Point contacts .............................................. 13

2 Introduction to Andreev reflection spectroscopy ............. 15
  2.1 Basic principle .............................................. 15
  2.2 Brief history ................................................ 18

3 Original and modified BTK theory ........................... 21
  3.1 The Bogoliubov-de Gennes equation ....................... 21
  3.2 Original BTK theory ........................................ 24
  3.3 Modification of the BTK theory ............................ 32
  3.4 Potential pitfall ............................................ 34

4 Experimental ....................................................... 37
  4.1 Some experimental approaches ............................. 37
  4.2 Tip-sample approach ....................................... 39
  4.3 Current-voltage measurement ............................... 44

5 Contact phase transition ....................................... 49
  5.1 Finite-bias conductance minima ............................ 49
  5.2 Westbrook-Javan Model ..................................... 53

6 Interface spin-flip scattering .................................. 57
  6.1 Test measurements ........................................... 57
  6.2 Decay of spin polarization .................................. 59
  6.3 Interface spin-flip scattering ............................... 62
# Part II Tunnel junctions

## 7 Introduction to spin-polarized tunneling

- 7.1 Normal metal-superconductor tunneling ........................................ 69
- 7.2 Conductance and density of states ............................................. 71
- 7.3 The effect of an applied magnetic field ....................................... 74
- 7.4 Brief history .............................................................................. 76

## 8 Theory of spin-polarized tunneling

- 8.1 Conductance and the BCS density of states ..................................... 79
- 8.2 Zeeman splitting and spin polarization .......................................... 81
- 8.3 Corrections on the BCS density of states ....................................... 83

## 9 Experimental

- 9.1 Junction preparation .................................................................... 89
- 9.2 Sorption-pumped $^3$He refrigerator ............................................ 95
- 9.3 Magnetization and alignment ...................................................... 98
- 9.4 X-ray photoelectron spectroscopy ............................................. 100

## 10 The superconducting electrode

- 10.1 The critical field ....................................................................... 105
- 10.2 Aluminum electrodes ............................................................... 109
- 10.3 Vanadium electrodes ............................................................... 116

## 11 Barrier dependence of tunneling spin polarization

- 11.1 Introduction ............................................................................. 119
- 11.2 AlO$_x$ and MgO barriers ......................................................... 122
- 11.3 TaO$_x$ and HfO$_x$ barriers ....................................................... 127
- 11.4 Conclusions and suggestions .................................................... 129

## 12 Thermal stability of tunneling spin polarization

- 12.1 Motivation .............................................................................. 131
- 12.2 Intrinsic thermal robustness ....................................................... 133
- 12.3 The role of Mn diffusion ........................................................... 137
- 12.4 Conclusions and suggestions .................................................... 140

## Bibliography

- 141

## Summary

- 149

## Samenvatting

- 153
List of publications 157

Over de auteur 159

Acknowledgements 161
Chapter 1

General introduction

The topic of this thesis is the direct measurement of the spin polarization in electron transport, the parameter that is responsible for the magnetoresistance effect in various layered magnetic structures. The research on spin polarization is not only essential for better fundamental understanding, but the wide application range of magnetoresistive devices makes it technologically relevant as well.

This general introduction briefly describes different magnetoresistance effects and their applications. Subsequently, the concept of spin polarization is defined, several fundamental aspects related to different types of currents are discussed, and the direct measurement techniques are introduced. This chapter ends with a rough outline of the work described in this thesis.

1.1 Magnetoresistive devices and applications

A magnetoresistive device is a device that shows a change in resistance under the application of a magnetic field. There are several different types of magnetoresistance, each having a different magnitude.

The resistance of any metal changes when a field is applied perpendicular to the direction of the current. This relatively small magnetoresistance, typically less than 0.1 %, originates from the increase in scattering as the electrons move in helical orbits due to the Lorentz force. A stronger effect is observed in ferromagnetic metals. The resistance of a ferromagnetic metal is dependent on the angle between the magnetization and the current. This magnetoresistance, referred to as anisotropic magnetoresistance (AMR), is typically several percent.

In 1988 the giant magnetoresistance (GMR) effect was discovered [1]. This effect is observed in a structure consisting of ferromagnetic layers separated by a nonmagnetic layer as shown in figure 1.1. Examples of GMR structures are Fe/Cr/Fe and Co/Cu/Co. The GMR effect is the increase in resistance when the magnetizations of the magnetic layers are switched from parallel to antiparallel. Typically the size of the effect is 10 % at room temperature. The GMR effect has enabled a significant improvement of hard-disk
read-head performance. Consequently, inductive and AMR-based read-heads have been replaced by GMR-based read heads.

Another relatively new and large magnetoresistance effect is the tunnel magnetoresistance effect (TMR). Here two ferromagnetic layers are separated by an insulator as shown in figure 1.2. Such a structure is referred to as a magnetic tunnel junction (MTJ). The insulator is thin enough, typically 1 nm, to allow for a quantum mechanical tunnel current to flow. As in GMR, the TMR effect is the increase in resistance when the magnetizations of the magnetic layers are switched from parallel to antiparallel. The effect was first observed in 1975 by Julliere in a Fe/Ge/Co junction [2]. Later, in 1995, Moodera et al. was able to obtain reproducible TMR effects of 10 to 20 % at room temperature with CoFe/AlO$_x$/Co junctions [3]. To date, AlO$_x$ has proven to be the most suitable insulator. With optimized junction preparation procedures and the proper choice of the material for the ferromagnetic layers, AlO$_x$-based junctions have a TMR effect of 70 % at room temperature [4].

Like GMR elements, MTJ’s have a high potential for industrial applications because of the large size of the TMR effect [5]. A MTJ is less suitable for use as a disk drive read head, however, because its larger resistance leads to a larger capacitive time constant and intrinsic noise level. The high and the low resistive magnetization states of a MTJ and
GMR element can be used to store information without the need of a power supply. Such a non-volatile memory device is referred to as a magnetic random access memory (MRAM). The memory consists of a two dimensional array of MTJ’s or GMR elements each serving as one bit. Reading is done by measuring the resistance and writing is performed with use of magnetic fields generated by adjacent current lines. In this application a GMR element is less suitable since its low resistance leads to a low voltage signal at the small read current required for compatibility with semiconductor technology.

**MRAM and Flash**

The major non-volatile solid state memory in use today is “flash electrical erasable programmable read only memory”, also known as flash EEPROM or flash. This type of memory is used in, for example, digital cameras and universal serial bus (USB) flash drives for the personal computer, often referred to as USB memory sticks. A memory cell of a flash memory is based on the floating gate transistor shown left in figure 1.3. The floating gate is capacitively coupled to the control gate and the source-drain channel. The logic bit is stored in the form of electric charge in the floating gate. This charge determines the threshold voltage for opening of the source-drain channel as shown right in figure 1.3. Programming and erasing the memory cell, i.e. charging and discharging the floating gate, is done by electron transport through the surrounding dielectric driven by a relatively high voltage. Under low voltage reading conditions, the charge remains stored for a period of years due to the high resistivity of the dielectric surrounding the floating gate.

Flash memory has several shortcomings. Programming and erasing consumes relatively high power due to the need of the high voltage. This makes it less suitable to be used in portable products, such as digital cameras and mobile phones, where low power consumption is important. Another shortcoming of flash is the programming speed. Information storage is slow because the high resistance of the dielectric and the capacitive coupling

![Figure 1.3: The floating gate transistor (left) is the basic element of a memory cell of a flash memory. The logic bit is stored in the form of electrical charge on the floating gate, which determines the control gate threshold voltage (right).](image)

\[\text{control gate voltage} \rightarrow \text{drain current} \begin{cases} \text{floating gate negatively charged} \\
\text{no charge on floating gate} \end{cases} \]
lead to unavoidable large time constants. Since it is expected that MTJ-based MRAM can overcome the speed and power shortcomings of flash memory [6–8], several companies are currently spending effort in developing MRAM.

It is clear from the previous discussion that the magnetoresistance effect of GMR elements and MTJ’s have a major impact on the industry of hard-disk read-heads and, possibly, future solid-state memories. Responsible for these effects is the spin polarization of the electric current, the parameter which is defined and discussed in the next section.

1.2 Spin polarization of an electric current

In general, an electric current can be regarded as a sum of two separate contributions, one from the spin-up electrons $J^\uparrow$ and one from the spin-down electrons $J^\downarrow$. When one contribution is larger than the other, the current is spin-polarized. The degree of spin polarization $P$ is defined as

$$P = \frac{J^\uparrow - J^\downarrow}{J^\uparrow + J^\downarrow}.$$  \hspace{1cm} (1.1)

By definition, the spin-up electrons are aligned with an applied magnetic field. Consequently, when $P$ is positive, the current is dominated by the spin-up electrons aligned with the field, and when $P$ is negative the current is dominated by spin-down electrons pointing against the field direction. When $P$ is 1 or -1, the current is fully spin polarized, i.e. carried only by spin-up or spin-down electrons. Equation (1.1) is the general definition of spin polarization and applies to any electrical current. It can, for example, be the current in a bulk ferromagnetic metal, the current crossing a ferromagnetic/nonmagnetic metal interface in a GMR element or point contact, or it can be the current tunneling through the barrier in a tunnel junction.

In the theories described later in this thesis, used to extract $P$ from current-voltage measurements, the polarization is incorporated by using equation (1.1). This definition, however, does not address the origin of the polarization. It is possible to deduce alternative expressions from equation (1.1) based on certain assumptions applying to specific situations [9]. We are going to consider some of these alternative expressions here since they provide a handle to identify different origins and to discuss several fundamental aspects of spin polarization.

Current in a bulk metal

The most simple case we can consider is the case of a current in a bulk metal. For such a current we can derive an expression for $P$ using Ohm's law, $J = \sigma \mathbf{E}$, where $J$ is the current density, $\sigma$ the conductivity, and $\mathbf{E}$ the electric field driving the electrons through the metal. When the electron system is described as a classical free electron gas, the conductivity is given by the Drude formula

$$\sigma = \frac{ne^2\tau}{m},$$  \hspace{1cm} (1.2)
where \( n \) is the electron density, \( e \) the electron charge, \( \tau \) the electron-lattice scattering time, and \( m \) the electron mass. A more realistic description of the electron transport is based on quantum theory. From this description it follows that not all the electrons are participating in the current but only those located at the Fermi level, and that the electrons at the Fermi level respond to the electric field as if their mass is different from the free electron mass. These two aspects can be incorporated in the Drude formula by replacing the electron density \( n \) with the density of states at the Fermi level \( \rho \), and the electron mass \( m \) with an effective mass \( m_{\text{eff}} \). With these modifications we can write for the current density

\[
J \propto \frac{\rho \ e^2 \ \tau}{m_{\text{eff}}} \ E.
\]

(1.3)

In a ferromagnetic metal, \( \rho \) and \( m_{\text{eff}} \) are dependent on the orientation of the electron spin due to the exchange interaction. The electron-lattice scattering time \( \tau \) is not dependent on the spin orientation since the electron-lattice interaction, i.e. the interaction with lattice defects, impurities and phonons, is a Coulomb interaction. Substitution into the general definition of spin polarization then results in

\[
P = \frac{\rho^\uparrow/m_{\text{eff}}^\uparrow - \rho^\downarrow/m_{\text{eff}}^\downarrow}{\rho^\uparrow/m_{\text{eff}}^\uparrow + \rho^\downarrow/m_{\text{eff}}^\downarrow} \quad \text{(current in bulk metal).} \tag{1.4}
\]

When the dependence of the effective mass on the spin orientation is neglected, the spin polarization simplifies to the polarization of the density of states

\[
P = \frac{\rho^\uparrow - \rho^\downarrow}{\rho^\uparrow + \rho^\downarrow} \quad \text{(density of states polarization).} \tag{1.5}
\]

We consider a few examples to discuss the role of the effective mass and other aspects of spin polarization [9, 11]. Figure 1.4-(a) shows a simplified density of states diagram of Fe. In the diagram two types of density of states (DOS) can be distinguished. The first type is the \( s \)-character DOS. Electrons with \( s \)-character can be regarded as free electrons with non-localized wave functions. The \( s \)-character energy bands, and accordingly the DOS, extend over a large energy range. The second type is the \( d \)-character DOS. The wave functions of \( d \)-character electrons are localized and the electrons have a large effective

<table>
<thead>
<tr>
<th>Total DOS</th>
<th>( s )-character (itinerant and mobile)</th>
<th>( d )-character (localized and heavy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Co</td>
<td>−</td>
<td>+</td>
</tr>
<tr>
<td>Ni</td>
<td>−</td>
<td>+</td>
</tr>
</tbody>
</table>
mass which makes them relatively immobile. The $d$-character energy bands are weakly dispersive, i.e. they occupy a relatively small energy range, resulting in a narrow but large contribution to the DOS. The spin-up and spin-down bands, predominantly the $d$-bands, are spin-split due to the exchange interaction. The total number of spin-up electrons is larger than the total number of spin-down electrons, resulting in a net magnetization in upward direction. This is conform the convention that the spin-up electrons are aligned with an externally applied magnetic field. For this reason the spin-up electrons are referred to as the majority electrons, and the spin-down as minority electrons. The major part of the spin-up $d$-character DOS in Fe is located at the Fermi level, while for spin-down it is located above the Fermi level. Consequently, $\rho^\uparrow$ is larger than $\rho^\downarrow$, i.e. the spin polarization of the total DOS is positive. In a more detailed analysis based on band structure calculations, the polarization of the $s$ and $d$-character DOS are considered separately. In Fe, both the $s$ and $d$-character DOS have a positive polarization [10] (see table 1.1), and, consequently, also the polarization of the current is positive [9].

Figure 1.4-(b) shows the simplified diagrams of the DOS in Co and Ni. In these metals the situation is more complicated. The major part of the $d$-character DOS of the spin-up electrons is located below the Fermi level, while for the spin-down electrons it is located at the Fermi level. This leads to a negative polarization of the total density of states in contrast to Fe. Like in Fe, however, the polarization of the $s$-character DOS is positive [10] (see table 1.1). Since the $s$-character electrons have a relatively small effective mass and, therefore, contribute more to the current than the $d$-character electrons, the polarization of the current in Co and Ni is not negative. Calculations indicate that the polarization
Chapter 1. General introduction

Figure 1.5: Simplified diagrams of the density of states representative for CrO$_2$ and NiMnSb (a), and La$_{0.7}$Sr$_{0.3}$MnO$_3$ (b).

of the current in Ni is essentially zero [9], and experiments with GMR elements indirectly indicate that the polarization of the current in Co is positive [12].

To end this discussion, two more examples are considered. Figure 1.5-(a) shows a simplified density of states diagram applying to CrO$_2$ and NiMnSb. These metals are special since their spin-down density of states at the Fermi level is zero, which makes the density of states at the Fermi level and, accordingly, the electric current fully spin-polarized. Such metals are denoted as half-metals. Figure 1.5-(b) shows a density of states diagram representative for La$_{0.7}$Sr$_{0.3}$MnO$_3$. The polarization of the density of states in this metal is relatively small, i.e. $\rho^\uparrow \approx \rho^\downarrow$. The spin-up electrons at the Fermi level, however, have a much larger effective mass than the spin-down electrons and therefore contribute less to the current. Thus, despite the absence of a significant polarization of the total density of states, a current can have a considerable degree of spin polarization due to a difference in the spin-up and spin-down effective mass.

Andreev reflection spectroscopy

As mentioned earlier, the spin polarization in a bulk ferromagnet can be deduced indirectly from GMR experiments [12]. In these experiments, the polarization is deduced from the change in the GMR effect observed by varying the appropriate layer thicknesses and the number of layers in a GMR element.

A direct measurement technique to measure the spin polarization of the current in a bulk metal is not available to date. There is one direct measurement technique, however, which measures not strictly the polarization of the current in the bulk metal, but the
polarization of a current that flows from the metal into a superconductor via a point contact. This technique is known as Andreev reflection spectroscopy and is illustrated in figure 1.6. The Andreev reflection spectroscopy technique is the topic of the first part of this thesis where it will be introduced further and explained in full detail. Despite the fact that the current is flowing through a point contact, the polarization measured by Andreev reflection spectroscopy can be considered as a good indication of the polarization in the bulk ferromagnet [9]. The technique, however, is not sensitive to the sign of the spin polarization, i.e. only the magnitude of the polarization can be measured.

Tunneling spin polarization

A different type of current we consider is the current consisting of electrons tunneling through the barrier of a tunnel junction. The transport mechanism responsible for tunnel current and the current in the bulk of a metal, have a completely different nature. Therefore the polarization of tunnel current should not be confused with the polarization given by equation (1.4). The polarization of tunnel current, or tunneling spin polarization, is responsible for the TMR effect of a magnetic tunnel junction.

The electrodes of a magnetic tunnel junction are both ferromagnetic. For simplicity we first consider a tunnel junction with one ferromagnetic and a nonmagnetic electrode. The ferromagnetic and nonmagnetic electrode will be denoted as electrode 1 and 2, respectively. At a given bias voltage, the number of electrons tunneling from electrode 1 to electrode 2 is proportional to the number of conduction electrons present in electrode 1, the tunnel probability $T$, and the number of empty electron states in electrode 2. At small bias voltage, both the number of conduction electrons and the number of empty electron states are proportional to the DOS of the electrode/barrier interfaces at the Fermi level. Accordingly, the tunnel current is proportional to the product of the DOS of the electrode/barrier interfaces at the Fermi level and the tunnel probability $T$, a result which will be derived
more formally in chapter 8. The DOS at the interfaces are different from the bulk of the electrodes due to the bonding between the atoms in the electrode and the barrier. To distinguish from the bulk DOS, which was denoted previously as $\rho$, the symbol $\sigma_1$ and $\sigma_2$ are used for the DOS at the interfaces. We thus can write

$$J \propto \sigma_1 \bar{T} \sigma_2$$  \hspace{1cm} (tunnel current).  \hspace{1cm} \text{(1.6)}$$

Substitution of this expression in the general definition of spin polarization leads to

$$P = \frac{\sigma^\uparrow \bar{T}^\uparrow - \sigma^\downarrow \bar{T}^\downarrow}{\sigma^\uparrow \bar{T}^\uparrow + \sigma^\downarrow \bar{T}^\downarrow}$$  \hspace{1cm} \text{(tunneling spin polarization),}  \hspace{1cm} \text{(1.7)}$$

where we have used that $\sigma^\uparrow_2 = \sigma^\downarrow_2$, since this electrode is non-magnetic, and written $\sigma_1$ simply as $\sigma$ keeping in mind that it is the Fermi level DOS at the ferromagnetic metal/barrier interface. This polarization is referred to as the tunneling spin polarization. Equation (1.7) tells us that the tunneling spin polarization not only arises from a difference in $\sigma^\uparrow$ and $\sigma^\downarrow$, but also from a spin-dependent tunnel probability. Accordingly, the polarization is not only determined by the ferromagnetic electrode but depends on the material used for the barrier as well.

**Direct measurement of tunneling spin polarization**

The tunneling spin polarization can be measured directly with the spin-polarized tunneling technique, illustrated in figure 1.7. This technique uses a superconducting counter electrode as a detector for the spin polarization, and is, therefore, also known as superconductor tunneling spectroscopy. The spin-polarized tunneling technique is the topic of the second part of this thesis where it will be introduced further and explained in full detail. In contrast to Andreev reflection spectroscopy, this direct measurement technique is sensitive to both the magnitude and the sign of the polarization.

![Figure 1.7: Illustration of the spin-polarized tunneling technique for direct measurement of the tunneling spin polarization. The technique is also referred to as superconducting tunneling spectroscopy.](image-url)
TMR and tunneling spin polarization

Previously we have considered the spin polarization of the tunnel current in a junction with one ferromagnetic and one nonmagnetic electrode. When the second electrode is also ferromagnetic, we need to distinguish between the two magnetization states. The magnetizations can be aligned parallel (P) and antiparallel (AP). Under the assumption that the spin orientation of the electrons is conserved during tunneling, the current in the parallel state can be written as

\[ J_P \propto \sigma_1^\uparrow T_1^{\uparrow\uparrow} \sigma_2^\uparrow + \sigma_1^\downarrow T_1^{\downarrow\downarrow} \sigma_2^\downarrow, \]  

in analogy to equation (1.6). To obtain the expression for the antiparallel state we reverse the magnetization direction of the second electrode, i.e. we reverse the spin which corresponds to the second electrode,

\[ J_{AP} \propto \sigma_1^\uparrow T_1^{\uparrow\downarrow} \sigma_2^\downarrow + \sigma_1^\downarrow T_1^{\downarrow\uparrow} \sigma_2^\uparrow. \]  

In the above equations the use of the four different tunnel probabilities is necessary since the tunnel probability from a majority to a majority state \( T^{\uparrow\uparrow} \), is not necessarily equal to the tunnel probability from a majority to a minority state \( T^{\uparrow\downarrow} \). Likewise, \( T^{\downarrow\downarrow} \) is not necessarily equal to \( T^{\downarrow\uparrow} \).

In general \( J_P \) is different from \( J_{AP} \), i.e. there is a tunnel magnetoresistance (TMR) effect. The magnitude of the TMR effect is defined as the difference in the antiparallel and parallel state resistances normalized by the parallel state resistance,

\[ \text{TMR} = \frac{R_{AP} - R_P}{R_P} = \frac{J_P - J_{AP}}{J_{AP}}. \]  

(1.10)

Note that it is also possible to normalize \( R_{AP} - R_P \) with \( R_{AP} \), leading to another definition of TMR. In literature, however, mostly the definition by equation (1.10) is used. By substitution of equations (1.8) and (1.9) into equation (1.10) one can express the TMR as

\[ \text{TMR} = \frac{2P_1 P_2}{1 - P_1 P_2}, \]  

(1.11)

where the polarizations \( P_1 \) and \( P_2 \) correspond to electrode 1 and 2, respectively. This result, known as the Julliere formula for TMR since it was derived earlier by Julliere [2], can be obtained only by writing the tunnel probability as a product of two probabilities, \( T^{\uparrow\uparrow} = T_1^{\uparrow} T_2^{\downarrow} \), \( T^{\uparrow\downarrow} = T_1^{\uparrow} T_2^{\uparrow} \), etc. In this way one considers the tunneling process as a two-step process via a virtual state in the barrier. \( T_1^{\uparrow} \) is the tunnel probability of a majority electron from electrode 1 to the virtual barrier state, \( T_2^{\uparrow} \) is the tunnel probability of a majority electron from the virtual barrier state to electrode 2, etc. Using this notation, we obtain

\[ P_1 = \frac{\sigma_1^\uparrow T_1^{\uparrow} - \sigma_1^\downarrow T_1^{\downarrow}}{\sigma_1^\uparrow T_1^{\uparrow} + \sigma_1^\downarrow T_1^{\downarrow}}, \] \[ \text{and} \] \[ P_2 = \frac{\sigma_2^\uparrow T_2^{\uparrow} - \sigma_2^\downarrow T_2^{\downarrow}}{\sigma_2^\uparrow T_2^{\uparrow} + \sigma_2^\downarrow T_2^{\downarrow}}. \]  

(1.12)
Chapter 1. General introduction

The Julliere formula reflects that the polarizations $P_1$ and $P_2$ are exclusively responsible for the TMR effect, which, as claimed earlier, emphasizes the importance of the tunneling spin polarization. The formula can be used to estimate $P_1$ and $P_2$ when the magnitude of the TMR effect is known. However, because of the subtle difference between the tunnel probabilities in equation (1.12) and (1.7), $P_1$ and $P_2$ are not strictly equal to the tunneling spin polarization measured in a spin-polarized tunneling experiment (for a related discussion see for example ref. [13]). For this reason, we will refer to $P_1$ and $P_2$ as the Julliere spin polarizations.

1.3 Outline of this thesis

This thesis is divided in two parts. The topic of part I is the Andreev reflection spectroscopy measurement technique, and the work described in part II is based on the spin-polarized tunneling technique.

The use of Andreev reflection spectroscopy for the direct measurement of spin polarization is relatively new and currently several aspects of this technique are unclear. The work described in part I is performed to provide explanations for several of these outstanding issues.

Spin-polarized tunneling is a well-established measurement technique. Only recently, however, the dependence of the tunneling spin polarization on the material used for the barrier is recognized. Direct experimental proof of this decisive role of the barrier material, however, is currently not available. In part II, experimental work is presented performed with a view to provide direct evidence for the barrier dependence. In addition to the barrier dependence, also the thermal stability of the tunneling spin polarization has been investigated. This work is performed especially to investigate a problem currently encountered in the development of MRAM.
Part I

Point contacts
Chapter 2

Introduction to Andreev reflection spectroscopy

This chapter explains the basic principle of the Andreev reflection spectroscopy technique and gives a brief review on its history. A fully qualitative theory and experimental details are described in chapter 3 and 4, respectively.

2.1 Basic principle

In Andreev reflection spectroscopy the spin polarization $P$ of the current flowing through a contact between a metal and a superconductor is measured. An example of such a contact is shown in figure 2.1. The current-voltage relation of the contact, or, more precisely, the conductance-voltage relation, is dependent on $P$. Consequently, $P$ can be deduced from a measurement of the conductance. The conductance at zero bias voltage is most dependent on $P$. Here the basic principle of this dependence is explained.

At small bias voltage, an individual electron in the normal metal (N) is not allowed to enter the superconductor (S) due to the presence of the energy gap in the single-electron...
states. It is possible, however, for the electron to enter the superconductor simultaneously with another electron of opposite spin by forming a Cooper pair. This conduction process is known as Andreev reflection [14], and is illustrated in figure 2.2-(a). After the Andreev reflection process, the two electrons have opposite momentum, as is required for formation of a Cooper pair. Conservation of momentum requires that on average one hole per incident electron is created, which travels back into the normal metal in a direction opposite to that of the incident electron, i.e. the incident electron is reflected as a hole. When all the incident electrons are Andreev reflected, the conductance of the N/S interface \( G_{NS} \) is twice the conductance of the N/N interface \( G_{NN} \) since the holes carry a positive charge in opposite direction to the negatively charged electrons. In other words, when the superconductor is switched from the superconducting state to the normal state, the conductance drops with a factor two,

\[
\frac{G_{NS}}{G_{NN}} = 2 \quad \text{(low bias,} \; P = 0)\]

The ratio \( G_{NS}/G_{NN} \) is referred to as the normalized conductance. When the normal metal is a ferromagnet with a degree of spin polarization, the probability for the electron to find a second electron with opposite spin is smaller and, accordingly, the Andreev reflection process is suppressed thereby lowering the conductance of the interface. In the extreme situation of full spin polarization, the conductance is zero since the Andreev reflection process is suppressed completely and the incident electron is only specularly reflected at the interface,

\[
\frac{G_{NS}}{G_{NN}} = 0 \quad \text{(low bias,} \; |P| = 1)\]

This situation is shown in figure 2.2-(b). The dependence of the zero bias conductance

**Figure 2.2:** Conduction across the N/S interface at low bias. The Andreev reflection process (a) is suppressed when the metal has a degree of spin polarization (b).
on the spin-polarization is the basis of the point contact Andreev reflection technique. The suppression of the Andreev reflection probability is linear dependent on the spin polarization. Interpolation between the two equations above leads to

$$\frac{G_{NS}}{G_{NN}} = 2(1 - |P|) \quad \text{(low bias)}.$$  

The suppression of the conductance by the polarization is not sensitive to the sign of the spin polarization. That is, it does not matter if there is a minority of spin-down or a minority of spin-up electrons. In both situations the Andreev reflection probability will be suppressed by an equal amount. Thus, in contrast with the spin-polarized tunneling technique, the sign of the polarization can not be measured.

When the bias voltage is increased to the energy gap in the superconductor, electrons start to enter the superconductor individually by occupying single-electron states as if the superconductor were a normal metal. When the bias voltage is increased further, the current is dominated by these individual electrons and $G_{NS}$ becomes equal to $G_{NN}$,

$$\frac{G_{NS}}{G_{NN}} = 1 \quad \text{(large bias)},$$  

As an example we consider the measured conductance-voltage curves shown in figure 2.3. The first measurement is performed by Ji et al. on a Pb/CrO$_2$ contact realized by pressing a superconducting Pb tip onto a CrO$_2$ sample [15]. Above 4 mV, the normalized conductance is equal to 1 in accordance with equation (2.4), while at zero bias the normalized conductance is almost zero. From the previous discussion we know that this can be explained only with a very high spin polarization of the current. With use of equation (2.3) a spin polarization of about 96 % can be deduced. The high polarization originates from the absence of minority electron states at the Fermi level in CrO$_2$ which was considered earlier in section 1.2 (see figure 1.5). The measurement of Ji et al. was the first experimental proof of the half-metallic band structure of CrO$_2$.

The second measurement shown in figure 2.3 is performed on a Nb/Cu contact obtained by pressing a superconducting Nb tip onto a Cu sample (see chapter 6). Since Cu is a non-magnetic material without spin polarization, we expect from the previous discussion that the normalized conductance at zero bias is 2. This is, however, not the case. When the bias is decreased, the normalized conductance increases, reaches a maximum at about 1.35 and shows a local minimum at zero bias. The discrepancy between equation (2.1) and figure 2.3 indicates that the previous discussion is oversimplified. Apparently, in contrast to what we assumed, at zero bias not all the incident electrons Andreev reflect. That is, there exists an additional mechanism which is able to suppress the Andreev reflection process, and, if not taken into account, potentially leads to an overestimation of the polarization. This mechanism is scattering at the N/S interface caused by imperfections such as impurities, lattice defects and roughness. Interface scattering is incorporated in the theory of Blonder, Tinkham and Klapwijk (BTK) [16]. In this theory the interface scattering is measured by a dimensionless parameter $Z$. The BTK theory does not include
spin polarization of the current, however, it can be straightforwardly modified. Both the original and the modified BTK theory are described in chapter 3. When the measured conductance curve is properly analyzed with the modified BTK theory, full agreement with experiment is obtained and, as expected for a Nb/Cu contact, zero polarization is extracted (see chapter 6).

### 2.2 Brief history

The principle of deducing the spin polarization from the conductance was originally proposed in 1995 by de Jong and Beenakker [17]. Three years later, Soulen et al. [18] were the first to report experimental results. As in most of the work published later by others, they obtained their contacts straightforwardly by pressing a superconducting tip onto a sample. Among other metals, they studied the 3$d$-ferromagnets Co, Ni, and Fe with a Nb tip. The spin polarization they report, however, is extracted only from the zero bias conductance by means of equation 2.3, which neglects interface scattering, and is, therefore, not very reliable. Furthermore, some of their measurements show anomalous behavior (see chapter 5).

Almost at the same time, Upadhyay et al. [19] obtained more reliable results with Co and Ni using a different experimental approach. To realize their contacts they used an insulating membrane with a hole of nanometer size, deposited the ferromagnet on one side and the superconductor Pd on the other side (see section 4.1). The analysis of their measurement is based on the BTK theory which includes scattering at the interface.

In 2001, Strijkers et al. published a straightforward extension of the BTK theory to include spin polarization of the current [20]. This modified BTK theory, similar to the...
Table 2.1: Spin polarization of different materials as measured with Andreev reflection spectroscopy. The asterisk (*) indicates that the contact is not obtained with a sample-tip approach, but from a membrane with a nanometer sized hole (see section 4.1).

<table>
<thead>
<tr>
<th>Material</th>
<th>$P$ [%]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co $^*$</td>
<td>37 ± 2</td>
<td>Buhrman [19]</td>
</tr>
<tr>
<td>Co</td>
<td>46 ± 3</td>
<td>Kant [21], Chien [20]</td>
</tr>
<tr>
<td>Fe</td>
<td>45 ± 3</td>
<td>Kant [21], Chien [20]</td>
</tr>
<tr>
<td>Ni $^*$</td>
<td>32 ± 2</td>
<td>Buhrman [19]</td>
</tr>
<tr>
<td>Ni</td>
<td>37 ± 2</td>
<td>Chien [20]</td>
</tr>
<tr>
<td>Ni$<em>x$Fe$</em>{1-x}$</td>
<td>45 ± 3</td>
<td>Nadgorny [22]</td>
</tr>
<tr>
<td>Gd</td>
<td>45 ± 4</td>
<td>Kant [21]</td>
</tr>
<tr>
<td>CrO$_2$</td>
<td>96 ± 2</td>
<td>Chien [15]</td>
</tr>
<tr>
<td>La$<em>{0.7}$Sr$</em>{0.3}$MO$_3$</td>
<td>75 ± 15</td>
<td>Nadgorny [23]</td>
</tr>
<tr>
<td>La$<em>{0.7}$Sr$</em>{0.3}$MO$_3$</td>
<td>78 ± 2</td>
<td>Chien [24]</td>
</tr>
<tr>
<td>La$<em>{0.6}$Sr$</em>{0.4}$MO$_3$</td>
<td>83 ± 2</td>
<td>Chien [24]</td>
</tr>
<tr>
<td>NiMnSb</td>
<td>58 ± 3</td>
<td>Nadgorny [18]</td>
</tr>
<tr>
<td>SrRuO$_3$</td>
<td>50 ± 8</td>
<td>Nadgorny [25], Raychaudhuri [26]</td>
</tr>
</tbody>
</table>

model used earlier by Upadhyay et al. and described in chapter 3, has become the standard for extracting the spin polarization.

In the last couple of years, Andreev reflection spectroscopy has been used to study various ferromagnetic metals. Table 2.1 gives an overview of the results. For a given ferromagnet, only the most recent and reliable results are included. In addition to the elemental 3$d$ transition metals, novel metals such as CrO$_2$, La$_{0.7}$Sr$_{0.3}$MO$_3$ and NiMnSb have been studied since, based on their calculated band structure, a large spin polarization of the current in these metals is expected (see section 1.2). To date, however, this has been experimentally established only for CrO$_2$ and La$_{0.7}$Sr$_{0.3}$MO$_3$.

A current issue of Andreev reflection spectroscopy is the unexplained systematic correlation between the extracted spin polarization and $Z$, the parameter that measures the interface scattering in the BTK theory [15, 20, 24]. An understanding of this correlation is lacking. The work described in chapter 6 of this thesis provides a quantitative model that explains this correlation by a loss of spin polarization due to spin-flip scattering.
Chapter 3

Original and modified BTK theory

Electron transport through a contact between a metal and a superconductor is described by the theory of Blonder, Tinkham and Klapwijk (BTK) [16]. This theory does not incorporate spin polarization. Strijkers et al. published an extension of the BTK model to account for spin polarization [20]. The modified BTK theory is used to extract the polarization from the measurement.

This chapter introduces the Bogoliubov-de Gennes equation, on which the BTK theory is based, describes the BTK theory and the modification. Additionally, it is pointed out that in some situations experimental data can be in false agreement with the modified BTK theory leading to incorrect extractions of spin polarization. This last subject is published in the form of a comment in Physical Review Letters [27].

3.1 The Bogoliubov-de Gennes equation

When a superconductor is cooled below its transition temperature, part of the electrons are paired into Cooper pairs. The unpaired electrons are referred to as quasi-particles. The quasi-particles are described by the Bogoliubov-de Gennes equation, in analogy to the description of electrons in a normal metal by the Schrödinger equation. In the BTK theory, the Bogoliubov-de Gennes equation is solved to find the reflection and transmission probabilities for electrons incident on the N/S interface. Subsequently, the probabilities are used to calculate the current at a given bias voltage. Before we describe the BTK theory, the Bogoliubov-de Gennes equation is introduced.

A quasi-particle is an electron which can be found in the two base-states “electron-like” and “hole-like”, which we will denote as $|e\rangle$ and $|h\rangle$, respectively. If the probability amplitudes to find the quasi-particle in $|e\rangle$ and $|h\rangle$ are $f(x,t)$ and $g(x,t)$, respectively, then the state of the quasi-particle can be described by the wave-function

$$\Psi(x,t) = f(x,t) |e\rangle + g(x,t) |h\rangle,$$

or

$$\Psi(x,t) = \begin{pmatrix} f(x,t) \\ g(x,t) \end{pmatrix}.$$  \hspace{1cm} (3.1)
The wave-function $\Psi$ obeys

$$i\hbar \frac{\partial \Psi}{\partial t} = \begin{pmatrix} H & \Delta \\ \Delta & -H \end{pmatrix} \Psi,$$

where

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - E_F + V(x).$$

Equation (3.2) is the Bogoliubov-de Gennes equation. This equation tells us that, apart from the coupling $\Delta(x)$, the quasi-particle obeys the Schrödinger equation when it is found in $|e\rangle$, and it obeys the time-reversed Schrödinger equation when it is found in $|h\rangle$. The substitution $\Psi(x, t) = \psi(x)e^{-i\omega t}$, where $E = \hbar\omega$, reduces equation (3.2) to

$$\begin{pmatrix} H & \Delta \\ \Delta & -H \end{pmatrix} \psi = E\psi,$$

since the Hamiltonian matrix is independent of time. Due to the offset $-E_F$, the energy $E$ is measured from the Fermi-level and is therefore referred to as the excitation energy of the quasi-particle.

To get acquainted with the Bogoliubov-de Gennes equation, and to identify the physical meaning of $\Delta$, we solve equation (3.4) for $V(x) = 0$ and a $\Delta$ independent of $x$. In the case $V(x) = 0$, the interaction between the quasi-particles and the lattice is neglected. For the trial solution

$$\psi = \begin{pmatrix} u \\ v \end{pmatrix} e^{ikx}$$

one finds that

$$E^2 = \left(\frac{\hbar^2 k^2}{2m} - E_F\right)^2 + \Delta^2.$$
energy gap of $2\Delta$ centered at the Fermi level. Thus, the energy $\Delta$ which was introduced as the coupling between the base-states $|e\rangle$ and $|h\rangle$, is half the energy gap at the Fermi level of a superconductor. For a typical elemental superconductor, $\Delta$ is several meV and $E_F$ several eV, i.e. $\Delta$ is roughly thousand times smaller than $E_F$. Therefore it should be noted that the magnitude of $\Delta$ as compared to $E_F$ in figure 3.1-(b) is exaggerated.

The BCS density of states

A special result of the BTK theory, to be discussed in the following section, is the correlation between the contact conductance and the well-known superconducting density of states, also referred to as the Bardeen, Cooper and Schrieffer (BCS) density of states [28]. As an introduction, we will calculate here the BCS density of states from equation (3.6) using elementary solid state physics.

In $k$-space the number of states $\rho(k)dk$ contained in a shell of radius $k$ and thickness $dk$ is given by

$$\rho(k)dk = \frac{V}{(2\pi)^3} \frac{4\pi k^2 dk}{4\pi k^2},$$

where $V$ is the volume of the metal, $V/(2\pi)^3$ the density of states in $k$-space and $4\pi k^2$ the area of a sphere with radius $k$ [29, 30]. From this equation, any density of states can be calculated by expressing $k$ and $dk$ in terms of energy by using a specific $E(k)$ relation. From figure 3.1-(b) we already know that the density of states is zero for $E < \Delta$. For $E > \Delta$ we use equation (3.6) and obtain

$$\rho_s(E)dE = \frac{V}{(2\pi)^3} \frac{4\pi \sqrt{2m^3}}{\hbar^3} \frac{(E + E_F)E}{E\sqrt{E + E_F}} dE \quad \text{for} \quad E > \Delta,$$
Figure 3.2: BCS quasi-particle density of states

where $\mathcal{E}$ is defined by $\mathcal{E}^2 = E^2 - \Delta^2$. For a normal metal $\mathcal{E} = E$ since $\Delta = 0$, which reduces equation (3.8) to

$$\rho_N(E) dE = \frac{\sqrt{2m^3}}{(2\pi)^3} \frac{4\pi}{\hbar^3} \sqrt{E + E_F} dE.$$  \hspace{1cm} (3.9)

This is the density of states of a free electron metal with its well-known square root dependence on energy. Normalization of $\rho_s$ by $\rho_N$ gives

$$\frac{\rho_s}{\rho_N} = \frac{(\mathcal{E} + E_F)E}{\mathcal{E} \sqrt{\mathcal{E} + E_F} \sqrt{\mathcal{E} + E_F}} \quad \text{for} \quad E > \Delta.$$  \hspace{1cm} (3.10)

As mentioned earlier, since $\Delta \ll E_F$ the bands, and accordingly the density of states, differ only from the bands in the normal metal on an energy scale small compared to $E_F$. This means that in the above expression, $E$ and $\mathcal{E}$ can be neglected with respect to $E_F$, which results in

$$\frac{\rho_s}{\rho_N} = \frac{E}{\mathcal{E}} = \frac{E}{\sqrt{E^2 - \Delta^2}} \quad \text{for} \quad E > \Delta.$$  \hspace{1cm} (3.11)

Figure 3.2 shows $\rho_s/\rho_N$ as a function of $E/\Delta$. The singular maxima at the energy gap edges are the characteristic feature of the density of states of a superconductor.

### 3.2 Original BTK theory

The theory of Blonder, Tinkham and Klapwijk (BTK) calculates the current-voltage relation of a point contact between a normal metal and a superconductor [16]. This section describes their calculation in full detail. The calculation can be divided in two parts. In the first part, equation (3.4) is solved to find the reflection and transmission probabilities
Chapter 3. Original and modified BTK theory

for an electron incident on the N/S interface. In the second part of the calculation these probabilities are used to arrive at an expression for the current at a given bias voltage. Before equation (3.4) is solved, the functions $\Delta(x)$ and $V(x)$ are specified.

**Specification of $\Delta(x)$**

In general, when a superconductor is in contact with a normal metal, Cooper pairs diffuse across the interface inducing superconductivity in N, and the normal metal has an effect on the superconductivity in S. The interaction between S and N is referred to as the proximity effect [31]. The proximity effect leads to a gradual variation of $\Delta$ on a certain length scale from zero in the normal metal to a constant value in the superconductor.

The BTK theory applies to the special case of a ballistic point contact, i.e. a contact with a contact radius much smaller than the electron mean free path. For such a contact it is allowed to neglect the proximity effect by assuming that $\Delta$ makes an abrupt step from zero at the N-side ($x < 0$) to a constant value at the S-side ($x > 0$).

**Specification of $V(x)$**

The BTK theory neglects the interaction between the quasi-particles and the lattice, i.e. $V(x) = 0$ in N and S, and it is assumed that the Fermi-energies in N and S are equal. Furthermore, the influence of the bias voltage on the potential $V(x)$ is neglected, which is allowed for bias voltages small compared to $E_F$.

As in the free electron approximation, any irregularity in the potential $V(x)$ leads to reflection, or scattering, probabilities. Therefore, in order to model the interface scattering due to, for example, roughness and impurities, one can use a potential $V(x)$ with a particular shape in the vicinity of $x = 0$. The disadvantage of using “more realistic” shapes for $V(x)$ is that it becomes impossible to solve the Bogoliubov-de Gennes equation analytically. For simplicity, allowing for an analytical solution, the BTK theory assumes a $\delta$-function with a strength $S$ localized at the interface, i.e. $V(x) = S\delta(x)$.

Although the use of the abstract $\delta$-function is theoretically advantageous, the interpretation of experimental results is not straightforward as will become clear in chapter 6.

**Calculation of reflection and transmission probabilities**

An electron incident on the N/S interface has a probability to undergo reflection and transmission processes. Figure 3.3 shows the incident electron and the reflected and transmitted particles as described in the BTK theory. The incident electron (probability 1) can undergo Andreev reflection, normal reflection, electron-like transmission and hole-like transmission. The probability amplitudes for these processes to occur are denoted as $a$, $b$, $c$ and $d$, respectively. In the normal metal the solution of equation (3.4) will have the form

$$
\psi_N(x) = 1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{i(k_F+k_N)x} + a \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{i(k_F-k_N)x} + b \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-i(k_F+k_N)x},
$$

(3.12)
Figure 3.3: Energy diagram illustrating an incident electron (1) along with the reflected (a and b) and the transmitted (c and d) particles. The reflected hole is represented as the reflected hole-like quasi-particle.

The reflected hole in the electron-like band with energy $-E$ and wave number $-(k_F-k_N)$, is represented as the reflected hole-like quasi-particle with energy $E$ and wave number $k_F-k_N$. In the superconductor the solution of equation (3.4) will have the form

$$\psi_s(x) = c \begin{pmatrix} u \\ v \end{pmatrix} e^{i(k_F-k_S)x} + d \begin{pmatrix} v \\ u \end{pmatrix} e^{i(-k_F+k_S)x},$$

(3.13)

The wave-numbers $k_N$ and $k_S$ are measured from the Fermi-wave number $k_F$. As required by the standard boundary conditions [32], the wave function is continuous

$$\psi_N(0) = \psi_S(0) \equiv \psi(0)$$

(3.14)

and its derivative obeys

$$\psi'_S(0) - \psi'_N(0) = S \frac{2m}{\hbar^2} \psi(0),$$

(3.15)

as is appropriate for a $\delta$-function potential with strength $S$. Equation (3.4) and the boundary conditions allow to solve for $a$, $b$, $c$ and $d$. The Andreev reflection probability $A$ and the normal reflection probability $B$ are given by $|a|^2$ and $|b|^2$, respectively. When $A$ and $B$ are known, the transmission probability, which is $C + D$, can be easily calculated since $A + B + C + D = 1$. We do not consider the details of the calculation, yet only consider the result for $A$ and $B$. The expressions for $A$ and $B$ are given in table 3.1. The expressions are written in a convenient form by using a dimensionless barrier strength $Z$, defined by

$$Z = \frac{k_F S}{2E_F} \quad \text{or} \quad Z^2 = \frac{1}{2} \frac{mS^2}{\hbar^2 E_F},$$

(3.16)

and the dimensionless parameter $\varepsilon$, defined by

$$\varepsilon = \frac{E}{\sqrt{E^2 - \Delta^2}}.$$

(3.17)
Chapter 3. Original and modified BTK theory

Table 3.1: The Andreev reflection probability $A$ and normal reflection probability $B$.

<table>
<thead>
<tr>
<th>$E &lt; \Delta$</th>
<th>$E &gt; \Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A = \frac{\Delta^2}{E^2 + (\Delta^2 - E^2)(1 + 2Z^2)^2}$</td>
<td>$A = \frac{\varepsilon^2 - 1}{[\varepsilon + (1 + 2Z^2)]^2}$</td>
</tr>
<tr>
<td>$B = 1 - A$</td>
<td>$B = \frac{4Z^2(1 + Z^2)}{[\varepsilon + (1 + 2Z^2)]^2}$</td>
</tr>
</tbody>
</table>

This parameter is equal to the BCS density of states deduced earlier.

Figure 3.4 shows the probabilities $A$ and $B$ as a function of $E$ for different values of $Z$. At sub-gap energies the incident electron cannot enter the superconductor as a quasiparticle, i.e. $A + B = 1$. Furthermore, for $Z = 0$ the only reflection is Andreev reflection, i.e. $A = 1$, while for a finite interface scattering strength $Z$, part of the incident electrons undergo normal reflection.

Next we consider some secondary results from the expressions for $A$ and $B$. At above-gap energies, the transmission $C + D$ equals $1 - (A + B)$. To find the transmission of the N/N interface we let $\Delta \to 0$, or $\varepsilon \to 1$. In this limit, evaluation of $1 - (A + B)$ gives

$$\text{transmission} = \frac{1}{1 + Z^2}, \quad (\Delta = 0). \quad (3.18)$$

This result is found in introductory quantum mechanics textbooks for the transmission of a $\delta$-function potential [32]. The Andreev reflection probability at the Fermi level $A(E = 0)$ is given by

$$A = \left(\frac{1}{1 + 2Z^2}\right)^2, \quad (E = 0), \quad (3.19)$$

which is roughly the square of equation (3.18). This is consistent with the fact that Andreev reflection requires simultaneous transmission of two independent electrons.

**Calculation of the current**

The known probabilities $A$ and $B$ are used to calculate the current at a given bias voltage. The current can be calculated in the normal metal or in the superconductor. For convenience it is calculated in the normal metal using the picture of an electron incident from the N-side introduced previously (figure 3.3). In the normal metal there are currents flowing to the right and to the left. The current flowing to the right consisting of the incident electrons with an energy in $[E, E + dE]$ is equal to

$$eA\nu(E)\rho(E)f(E)dE, \quad (3.20)$$
Figure 3.4: Probability for Andreev reflection (top) and for normal reflection (bottom). The probabilities are calculated with values of $Z$ of 0.00, 0.25, 0.50 and 1.25. The arrows indicate the trend with increasing $Z$. 
where $e$ is the charge of the electron, $A$ the area of the N/S interface, $v(E)$ the electron velocity, $\rho(E)$ the density of states and $f(E)$ the Fermi distribution function. Note that $\rho(E)f(E)dE$ is the density of electrons with an energy in $[E, E + dE]$. The part $A(E)$ of the incident electrons is Andreev reflected as holes. Accordingly the additional current

$$eAv(E)\rho(E)A(E)f(E)dE$$

(3.21)

flows to the right. The part $B(E)$ of the incident electrons is reflected normally, resulting in a current

$$eAv(E)\rho(E)B(E)f(E)dE$$

(3.22)

flowing to the left. There is a second current flowing to the left originating from particles incident from the S-side. This current can be written as

$$eAv(E)\rho(E)X(E)f(E)dE.$$  

(3.23)

In absence of an externally applied bias voltage, the total current is zero, implying that $X = 1 + A - B$.

In general, when a bias voltage is applied, non-equilibrium particle distributions will be generated and it is formally not allowed to use the Fermi distribution function. For the special case of a ballistic point contact, however, the equilibrium Fermi distribution function $f(E)$ can be used since the electrons are scattered far away from the contact and the probability that an incident electron is perturbed by another electron participating in the transport is negligible. With the convention that the bias voltage $V$ raises the energy of the normal metal by $eV$ with respect to the superconductor, the incoming electrons from the N-side have the distribution $f(E - eV)$ and the particles incident from the S-side have the distribution $f(E)$. Thus, for obtaining the current for a given bias voltage, we should replace $f(E)$ in expressions (3.20), (3.21) and (3.22) by $f(E - eV)$. Accordingly, the current resulting from electrons incident from the N-side is given by

$$eAv(E)\rho(E) [1 + A(E) - B(E)] f(E - eV)dE$$

(3.24)

and the current resulting from particles incident from the S-side is given by

$$eAv(E)\rho(E) [1 + A(E) - B(E)] f(E)dE,$$

(3.25)

where we have used that $X = 1 + A - B$. The total current becomes

$$I = eAv(E)\rho(E) [1 + A(E) - B(E)] [f(E - eV) - f(E)] dE.$$  

(3.26)

The function $f(E - eV) - f(E)$ is nonzero only in a region of size $eV$ in the vicinity of the Fermi level. Since $eV \approx \Delta \ll E_F$, the velocity and the density of states of the normal metal can be taken as constants and can be moved in front of the integral,

$$I = eAv\rho [1 + A(E) - B(E)] [(f(E - eV) - f(E)] dE.$$  

(3.27)
where now $v$ and $\rho$ are the electron velocity and density of states of the normal metal at the Fermi level, respectively. The conductance $G_{NS} = dI/dV$ then becomes

$$G_{NS} = -e^2 Av\rho \int [1 + A(E) - B(E)] f'(E - eV) dE,$$

(3.28)

where $f'$ is the derivative of the Fermi distribution function. The function $-f'(E)$ is zero everywhere except near $E = 0$ where it has a pulse-shape similar to a delta-function with a width proportional to $k_B T$. When both sides of the interface are normal metal ($\Delta = 0$), equation (3.28) reduces to

$$G_{NN} = \frac{e^2 Av\rho}{1 + Z^2},$$

(3.29)

since $A = 0$ and $1 - B = 1/(1 + Z^2)$. The conductance in the superconducting state normalized by the conductance in the normal state becomes

$$\frac{G_{NS}}{G_{NN}} = -(1 + Z^2) \int [1 + A(E) - B(E)] f'(E - eV) dE,$$

(3.30)

which is the main result of the BTK theory.

Figure 3.5 shows the normalized conductance for $\Delta = 1.5$ meV at 4.2 K and 1.5 K calculated with different values of $Z$. At low bias the normalized conductance equals 2 for $Z = 0$. This is the $P = 0$ result mentioned earlier in the first description of section 2.1, where it was assumed that all incident electrons Andreev reflect. When the interfacial scattering strength $Z$ increases, not all electrons Andreev reflect but an increasing part undergoes normal reflection. The suppression of Andreev reflection causes a local minimum in the zero bias conductance. The conductance maxima mark the edge of the superconducting energy gap.

The conductance calculated with large $Z$ is reminiscent of the BCS density of states. In fact for $Z \gg 1$ the Andreev reflection probability $A$ is zero and

$$B \approx \frac{Z^4}{\varepsilon Z^2 + Z^4} = \frac{1}{1 + \frac{\varepsilon}{Z^2}} \approx 1 - \frac{\varepsilon}{Z^2} \quad (Z \gg 1),$$

(3.31)

which reduces equation (3.30) to

$$\frac{G_{NS}}{G_{NN}} = -\int \frac{\rho_S}{\rho_N} f'(E - eV) dE \quad (Z \gg 1).$$

(3.32)

This result is exactly what is obtained when one calculates the current-voltage characteristic of a tunnel junction (see chapter 8).
Figure 3.5: The normalized conductance of an N/S contact calculated with the BTK theory (equation (3.30)) with values of $Z$ of 0.00, 0.25, 0.50, 0.75 and 1.25, for temperatures 4.2 K (top) and 1.5 K (bottom). The arrows indicate the trend with increasing $Z$. 
3.3 Modification of the BTK theory

The BTK theory described previously does not incorporate spin polarization. This section describes the modification to include spin polarization published by Strijkers et al. [20].

When the current $I$ has a degree of spin polarization $P$, it can be considered as a superposition of a fully polarized current $PI$ and a non-polarized current $(1 - P)I$. Here we assume $0 \leq P \leq 1$ for simplicity. The non-polarized current can be calculated in the same way as is done in the original BTK theory, i.e. with equation (3.30), and the fully polarized current can be calculated similarly but with use of modified probabilities $\tilde{A}$ and $\tilde{B}$. This leads to

$$\frac{G_{NS}}{G_{NN}} = -P(1 + Z^2) \int [1 + \tilde{A} - \tilde{B}(E)] f'(E - eV)dE$$

$$- (1 - P)(1 + Z^2) \int [1 + A(E) - B(E)] f'(E - eV)dE$$ (3.33)

The modified probabilities are determined as follows. Since the fully polarized current is carried by electrons of one spin species only, Andreev reflection cannot occur, i.e. $\tilde{A} = 0$ and $\tilde{B} + \tilde{C} + \tilde{D} = 1$. At energies smaller than $\Delta$, there can be no transmission, implying $\tilde{B} = 1$. To find $\tilde{B}$ for energies larger than $\Delta$, the modification assumes that the ratio between normally reflected and transmitted electrons is independent of the spin polarization, i.e.

$$\frac{\tilde{B}}{C + D} = \frac{B}{C + D},$$ (3.34)

which implies,

$$\tilde{B} = \frac{B}{1 - A} \quad (|E| > \Delta).$$ (3.35)

A rigorous calculation of Mazin et al. has shown that the assumption is essentially true [33, 34].

Equation (3.33) represents the modified BTK theory and is used to extract $P$ from the measurement. Figure 3.6 shows examples of the normalized conductance calculated with different $P$ and $Z$. In case of $Z = 0$, the situation of an ideal interface, the normalized conductance at zero bias is given by $2(1 - P)$, which is the result found earlier in section 2.1.
Figure 3.6: The normalized conductance of an N/S contact calculated with the modified BTK theory (equation (3.33)) with $Z = 0.00$, 0.25 and 0.50, and $P = 0.0, 0.2, 0.4, 0.5, 0.8$ and 1.0. The arrow indicates the trend with increasing $P$. 
3.4 Potential pitfall

As illustrated by the calculated curves in figure 3.6, the zero bias conductance is suppressed by two mechanisms, a suppression of Andreev reflection due to a degree of spin polarization, and a suppression of Andreev reflection due to interfacial scattering. It is important to notice that the curves for large $P$ look very similar to the curves in figure 3.5 calculated with large $Z$ and $P = 0$. This similarity can potentially lead to a misinterpretation of experimental data, more specific, the suppression of the sub-gap conductance may be incorrectly attributed to a high degree of spin polarization.

To demonstrate this pitfall, we consider as an example the two conductance curves shown in figure 3.7. The curves are measured from identically prepared Co/Al$_2$O$_3$/Al tunnel junctions, well below the superconducting transition temperature of aluminum. In both junctions the transport is governed by the Al$_2$O$_3$ tunnel barrier. Junction (a) shows the shape of the BCS superconducting density of states with zero conductance at zero bias and maxima at the edge of the superconducting energy gap. Junction (b), however, shows merely a suppression of the sub-gap conductance without signature of maxima at the energy gap edge. This shape is caused by a poorly developed superconducting density of states, probably due to limited structural quality of the aluminum electrode. By naively ignoring the tunneling transport, fair agreement with the modified BTK theory (solid line) can be obtained. In this case, the best fit is obtained with a spin polarization of 76 %, which is a clear overestimation of the 46 % found for Co with Andreev reflection spectroscopy (see table 2.1).

As another example we consider a conductance curve measured by Braden et al. from

![Figure 3.7](image)

**Figure 3.7:** Conductance of two Co/Al$_2$O$_3$/Al junctions measured at 0.3 K. A naive fit of the modified BTK theory (solid line) to the conductance of junction (b) incorrectly suggests a high degree of spin polarization.
a $\text{Ga}_{0.95}\text{Mn}_{0.05}\text{As}/\text{Ga}$ junction [35] very similar to curve (b) of figure 3.7. They attribute the suppression of the sub-gap conductance solely to a suppression of Andreev reflection due to a spin polarization of 85%. Although this high degree of spin polarization is in accordance with tunnel magnetoresistance [36] and recent spin-LED experiments [37], their interpretation of the conductance suppression is questionable. It is well-known that a Schottky tunnel barrier is present at the doped-GaAs/metal interface [38]. Therefore, the suppressed sub-gap conductance may simply be a signature of tunneling transport in combination with a poorly developed superconducting density of states of the Ga electrode.
Chapter 4

Experimental

The measurements presented in this thesis are performed with two home-build experimental setups. The setups are based on the so-called tip-sample approach, meaning that the point contacts are made by lowering a superconducting tip onto a sample. Before the mechanical and cryogenic aspects of these setups are described, we will briefly look at some other approaches for realizing point contacts. The chapter ends with a description of the electronics used for the measurement.

4.1 Some experimental approaches

The point contacts considered in this thesis are obtained with a tip-sample approach. Before this approach is explained, we first describe two other approaches for realizing point contacts.

Membrane with nano-hole

The publication by Upadhyay et al. describes one of the first Andreev reflection spectroscopy measurements [19]. A schematic of their N/S point contacts is shown in figure 4.1. The contact is based on a Si₃N₄ membrane which contains a hole with a diameter of 10-50 nm [39]. The membrane is obtained by chemical vapor deposition of 50 nm thick Si₃N₄ on a Si wafer followed by removal of a Si window by etching. The pattern of the nano-hole is transferred to the membrane by electron-beam lithography. The hole is created by a marginal dry etch just breaking through the membrane so that the far side opening is smaller than that actually patterned. Finally, the N/S contact is realized by depositing N on one side and S on the other side of the membrane.

Mechanical break junctions

A relatively successful approach for realizing point contacts is by means of the so called mechanical break junction technique [40]. Because of the high stability achieved, the tech-
technique has enabled exploration of various aspects of transport through atom-sized contacts. Mechanical break junctions, however, allow only for formation of contacts between two identical metals and, therefore, can not be used to create a N/S point contact as required for Andreev reflection spectroscopy. Nevertheless, the mechanical break junction will be briefly discussed below.

The break junction consists of a metallic wire attached to an elastic substrate with two droplets of epoxy as shown in figure 4.2. The wire is notched in between the two droplets by a knife. With use of a driving rod, the substrate is bent and consequently the wire is broken. After the break, the electrodes are brought back in contact and the contact area is controlled with a piezoelectric actuator mounted in line with the driving rod.

The success of mechanical break junctions originates from their extremely high stability, which is a result of a combination of two factors. First, the distance between the epoxy droplets can be made as small as 1 mm. This drastically reduces the sensitivity of the distance between the electrodes for external vibrations. Second, the wire is broken while the break junction is immersed in liquid helium. After the break, the metallic electrodes do not get contaminated or oxidized since the liquid helium constitutes a good vacuum. Additionally, the low temperature freezes out atomic motion at the surface of the electrodes which contributes to the stability of the contact.
4.2 Tip-sample approach

The results presented in this thesis are obtained by means of a straightforward approach in which a superconducting tip is mechanically lowered onto a ferromagnetic sample.

In designing an experimental setup for formation of point contacts by this approach, one needs to consider two important issues. The first issue involves the vacuum conditions at which the sample and tip are kept. Clean metallic surfaces are preserved when sample and tip are kept under vacuum at all time, that is, during preparation, mounting and cool-down. We will refer to this as \textit{in-situ} preparation. When sample and tip are exposed to air before they are mounted in the cryogenic system, their surfaces are oxidized and contain contaminations. This preparation will be referred to as \textit{ex-situ} preparation.

The second issue is the controllability of the tip movement. When sample and tip are isolated from vibrations, the controllability of the tip movement determines the amount of structural damage of tip and sample during contact formation. The tip can be moved, for example, with piezoelectric actuators, providing for a relatively fine controllability, or the tip can be moved using a straightforward mechanical mechanism such as a micrometer screw.

Apart from the work of Upadhyay \textit{et al.} (see previous section), all published work on the measurement of spin polarization with point contact Andreev spectroscopy (see section 2.2) is based on the tip-sample approach with \textit{ex-situ} preparation of tip and sample, and mechanical control of the tip. The experimental results presented in this thesis are obtained with \textit{ex-situ} preparation and two home-build low temperature point contact setups, which differ in the method used to control the tip movement. In the one described first, the tip is moved using piezoelectric actuators and in the second setup, a simple mechanical mechanism is used similar to that of other research groups.

Setup with piezoelectric tip movement

The motivation of using a piezoelectric actuator is the extremely fine controllability of the tip movement. Typically, the length of a 5 cm piezoelectric actuator changes by several nm when 100 mV is applied across its electrodes. Accordingly, when the system is isolated from vibrations, the distance between sample and tip can be controlled on an angstrom scale.

A schematic overview of the setup is shown in figure 4.3 and details can be found in ref. [41]. The heart of the setup consists of the coarse and fine piezo. The coarse piezo moves the sample holder towards the tip using a so-called stick-slip method. This coarse approach procedure stops when a tunnel current between sample and tip is detected. In this tunnel regime the bias voltage is several 100 mV and the tunnel current is kept constant at, for example, 1 nA by controlling the tip-sample distance with the fine piezo. Such a constant current mode is generally used during operation of a scanning tunneling microscope. After the coarse approach procedure the metallic contact is made by switching off the controller and lowering the tip with the fine piezo. The isolation against external
vibrations consists of the mass-spring system inside the experimental vacuum chamber, and the external suspension of the cryostat.

**Setup with mechanical tip movement**

The second home-build setup for making point contacts at low temperature uses a straightforward mechanical mechanism to press the tip onto the sample. As mentioned earlier, a similar mechanical approach is used by most other research groups [18, 20, 42]. The setup,
schematically shown in figure 4.4, is relatively simple as compared to the setup with piezoelectric tip movement.

The tip is fixed to a brass strip which acts like a spring. The strip can be bend by a manually driven rod which slides along the strip. The bending movement pushes the tip onto the sample. The brass strip is soldered onto the brass base of the system, which is in turn soldered at the end of a stainless steel tube. This tube facilitates the feed through of wiring and the driving rod. The width of the system is 1 cm, small enough for it to fit in the opening of a liquid helium transport vessel. Sample and tip can be cooled from room temperature to 4.2 K in several minutes by slowly sliding the tube into the helium vessel.

It should be noticed that in contrast to the previous setup no special measures are taken to isolate sample and tip from external vibrations. Still, the contact stability obtained is comparable to that of the previous setup. Apparently, extra measures for vibration isolation are not crucial. This can be explained by the dimensions of the system, which are about ten times smaller than those of the piezoelectric system. As mentioned earlier in the description of the mechanical break junction, a smaller system has a reduced sensitivity for external vibrations. Furthermore, as will be explained below, the oxides present on tip and sample also add to the stability of the contact.

Due to its short cool-down time, the setup with mechanical tip movement is more convenient to use. As a result, the larger part of the results are obtained using this setup.
Preparation of tip and sample

The superconducting tips are prepared from Nb or Pb wire. These elemental superconductors have a relatively high transition temperature (9.5 and 7.2 K, respectively). With these superconductors, the temperature provided by the helium bath cryostat and transport vessel (1.5–4.2 K) is low enough to perform the measurements. Different methods can be used to prepare the tip, however, as will be explained later, the preparation method is not of crucial importance.

The Nb tips are prepared simply by cutting a wire under grazing angle with scissors. From the field of scanning tunneling microscopy, it is known that with brittle metals this method can result in atomically sharp tips. For the Pb tips a method is used which makes use of the low melting temperature of Pb. A sharp tip is created by solidification when a Pb wire is slowly retracted out of liquid Pb. The Pb can be melted simply with a soldering iron.

The studied samples (Au, Cu, Al, Co, Fe and Gd) are either sputter-deposited films with a thickness of 30 to 50 nm, or bulk samples with a mechanically polished surface.

Model of the contact formation process

As tip and sample are kept in air before they are mounted and cooled down, oxides are formed on the surface. Here a model of the contact formation process is described, explaining the role and consequences of these oxide layers.

When tip and sample are brought together for the first time after cool-down, the insulating oxides prevent for a measurable tunnel current to flow. That is, tip and sample are in physical contact before a tunneling current can be detected. This conclusion is drawn simply from the significant physical deformation of tips observed before a tunnel current could be detected. Consequently, when a tunnel current is detected the sample and predominantly the tip are physically deformed. A simplified illustration of this situation is shown in figure 4.5-(a). Probably, the oxide layers are broken at several locations during deformation.

![Figure 4.5: Illustration of the tip and sample with oxidized surface during contact formation.](image-url)
since, especially at low temperature, the oxides are hard and brittle. The consequence of this unavoidable deformation of the tip is that the method chosen for preparing the tip is not very crucial.

In order to achieve a metallic contact, the oxide layers can be broken by pressing the tip further into the sample or by electrical breakdown achieved by a short voltage pulse with a magnitude of several volt. The contacts obtained by breakdown are more likely to show agreement with the BTK theory. During breakdown, one or more metallic paths are formed and the atoms of the tip and sample probably interdiffuse to some extent. An illustration of a metallic contact formed by electrical breakdown is shown in figure 4.5-(b).

Thus, due to the breakdown process, which is necessary because of the oxide layers, the S/N interface is rather undefined. An advantage of the presence of the oxides, however, is that the physical contact area is larger than the electric point contact area, which adds to the stability of the contact.

**Clean surfaces and no deformation**

Due to the oxides and the physical damage of the sample, certain experiments are not possible with use of the two setups described previously. An example is the study of spin polarization of a ferromagnetic single-crystal for different crystallographical orientations as illustrated in figure 4.6-(a). Another example, illustrated in figure 4.6-(b), is the study of the decay of spin polarization in a nonmagnetic metal by measuring as a function of nonmagnetic capping layer thickness.

To perform such experiments, clean interfaces and negligible damage during contact formation, i.e. *in-situ* preparation and controllability of the tip on a sub-angstrom scale, are required. A setup which provides for these requirements is a high-vacuum system equipped with a preparation chamber and a low temperature scanning tunneling microscope.

In december 2003 a commercially available ultra-high vacuum system, equipped with deposition facilities and a low temperature scanning tunneling microscope, has been in-

![Figure 4.6: Examples of Andreev reflection experiments possible only with clean surfaces and in absence of physical deformation.](image)
stalled in the group Physics of Nanostructures of the Eindhoven University of Technology. When one wants to use the microscope for measurement of metallic point contacts, two modifications are needed. The microscope is designed for measuring relatively small tunnel currents (typically below 500 nA). With the tip in metallic contact with the sample, the contact resistance can be as small as several Ω and the current is relatively large (mA range). To cope with this current, the electronics needs to be adapted. Furthermore, to measure the contact resistance correctly, additional wiring should be implemented to realize a four-point measurement (see section 4.3).

4.3 Current-voltage measurement

This last section is a description of the electronics used for the current-voltage and, more importantly, the conductance-voltage measurement.

Four-point measurement

The current-voltage (I-V) characteristic of the point contact is measured using a four-point configuration. A straightforward four-point configuration is shown in figure 4.7-(a). The voltage source is used to sweep the voltage and current is measured with the ammeter. The current flows through the leads and contacts on tip and sample. The resistance of the leads and the contacts are not negligible small as compared to the point contact resistance, resulting in parasitic voltage drops in series with the point contact. To exclude these parasitic voltage drops, the voltage between sample and tip is measured directly with a volt-meter using two extra leads and contacts on tip and sample. The essence of the four-point measurement is the fact that there is no current flowing through the extra leads so that the volt-meter measures the true bias voltage between tip and sample.

![Four-point measurement](image)

Figure 4.7: Four-point configuration using a volt-meter for measurement of the bias voltage (a) or using feedback for control of the bias voltage (b).
The measurements presented in this thesis are not performed with use of a straightforward voltage source as in figure 4.7-(a). Instead, a self-build voltage source is used which controls the bias voltage by using the voltage between tip and sample as feedback signal. This bias voltage controller, shown in figure 4.7-(b), ensures that the bias voltage is equal to the voltage requested by the experimenter. The advantage of the controller is that during the sweep only reading of the current signal is necessary. The bias voltage controller is described in more detail later in this section.

The lock-in technique

The derivative of the current-voltage characteristic \( \frac{dI}{dV} - V \), referred to as the conductance-voltage characteristic, is measured simultaneously with use of a lock-in technique. The basic concept of this technique becomes clear in the following brief discussion.

If \( I(V) \) is the current through the contact at bias voltage \( V \), then the current at a somewhat larger bias voltage \( V + dV \), can be expressed as

\[
I(V + dV) = I(V) + \frac{dI}{dV} dV + \ldots
\]

When \( dV \) is an ac modulation voltage equal to \( v \sin \omega t \) superimposed on the dc bias voltage, the above expression becomes

\[
I(V + v \sin \omega t) \approx I(V) + \frac{dI}{dV} v \sin \omega t.
\]

This means that due to the small modulation voltage the current signal contains a small ac component with an amplitude proportional to the conductance. This ac amplitude in the current signal is measured by a lock-in amplifier.

Basically, a lock-in amplifier is a volt-meter sensitive for signals at one specific frequency only. The lock-in amplifier multiplies the current signal (4.2) with the ac modulation voltage \( v \sin \omega t \), and passes this product through a low-pass filter. This operation averages out all components present in the current signal with a frequency different from \( \omega \). Additionally, it averages out signals which do have a frequency \( \omega \) but are not in phase with the ac modulation voltage.

Since the ac modulation amplitude \( v \) has a finite magnitude, the output signal of the lock-in amplifier is the average value of \( dI/dV \) in the voltage range \([V - v, V + v]\). Accordingly, features smaller than \( 2v \) are averaged out and features larger than \( 2v \) are resolved. Thus, when \( v \) is chosen arbitrary large, the smallest features may not be resolved. On the other hand, when \( v \) is arbitrary small, also the ac component present in the current signal is small and accordingly the noise in the measured conductance curve is unnecessary large.

In general, the smallest voltage scale on which features are visible is determined by thermal broadening of the Fermi level. There are exceptions however, for example when phase transitions are involved (see chapter 5), but these are not considered here. The
Table 4.1: Bias voltage scale of the smallest features in a current-voltage measurement

<table>
<thead>
<tr>
<th>sample temperature</th>
<th>voltage scale</th>
<th>modulation voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>room temperature (300 K)</td>
<td>100 mV</td>
<td>10 mV</td>
</tr>
<tr>
<td>liquid $^4$He (4.2 K)</td>
<td>1 mV</td>
<td>100 µV</td>
</tr>
<tr>
<td>pumped liquid $^3$He (0.3 K)</td>
<td>100 µV</td>
<td>10 µV</td>
</tr>
</tbody>
</table>

Width of the Fermi level is roughly $3.5kT$ (where $k$ is Boltzmann’s constant), which is about 300 µeV/K. Table 4.1 shows the smallest voltage scale on which features are visible for different temperature regimes. The table also suggests the appropriate magnitude of the ac modulation voltage.

Four-point measurement in more detail

In this last subsection we will have a look at the four probe measurement, introduced by figure 4.7-(b), in more detail. The electronics is shown schematically in figure 4.8. The bias voltage controller consists of the differential amplifier, the substractor and the integrator. The difference between the “input voltage” (defined in the figure), and 1000 times the bias voltage, is the input signal of the integrator. When this signal is not zero, the integrator increases or decreases the current through the contact until the bias voltage becomes equal to the input voltage divided by 1000. The bias voltage is controlled on a time scale roughly given by the time constant of the integrator divided by 1000, which is fast enough to keep up with the ac modulation voltage (typically a modulation frequency in between 200 and 300 Hz is used).

A standard analog output of a computer with a range of ±10 V and 5 mV resolution is used as the source for the dc input voltage. The factor 1000 gives a desired bias voltage range of ±10 mV and 5 µV resolution. The analog output of the computer is passed through a 20 Hz low-pass filter in order to remove unwanted noise. The ac modulation voltage is provided by the internal oscillator of the lock-in amplifier, and superimposed on the dc bias voltage with an adder. The ampèreme-meter, which is actually a current-to-voltage converter, sends the current signal to an analog input of the computer and the lock-in amplifier for reading the dc current and measurement of the conductance, respectively.

The setup described in this paragraph was developed with the intention to measure the relatively large effects in the conductance curve encountered in point contact Andreev reflection spectroscopy. The electronics is also successfully used for the spin-polarized tunneling measurements described in part II of this thesis, where the effects in the conductance curve are large as well. The electronics contains operational amplifiers which are not perfectly linear. These non-linearities have negligible influence on the measurements presented in this thesis. However, for the study of extremely small changes on top of an
essentially constant conductance, the non-linearities are significant and obscure the measurement. Usually, in such studies the use of operational amplifiers is avoided and only perfectly linear passive elements (batteries, inductors) are used.
Chapter 5
Contact phase transition

The conductance of S/N point contacts can be qualitatively different from the curves calculated with the BTK theory. This chapter explains a mechanism responsible for such anomalous conductance curves, and shows that anomalies can give insight in the microscopic geometry of the point contact.

The work described in this chapter can be considered as a generalization of the earlier work of Westbrook and Javan [43].

5.1 Finite-bias conductance minima

The conductance of S/N contacts may show a behavior that cannot be explained with the BTK theory. Anomalous behavior is observed at zero bias and at finite bias voltage (see for example refs. [44, 45]). Here we only consider anomalies at finite bias. In general, the finite-bias anomalies are one or more conductance minima. An example is shown in figure 5.1. The curve is measured by Soulen et al. on a Nb/Cu contact at 1.6 K [18].

Figure 5.1: Anomalous conductance of a Nb/Cu contact measured at 1.6 K. Taken from Soulen et al. [18].
The measurement has little resemblance with the conductance curves calculated with the BTK theory. In their paper, Soulen et al. do not address the origin of the anomalous conductance.

**Basic explanation**

Conductance minima as shown in figure 5.1 can be explained by a phase-transition of the contact from the S/N state to the N/N state induced by a combination of Joule heating and the magnetic field generated by the current. How the phase transition affects the conductance of the contact is qualitatively explained in figure 5.2. The top graph shows the current and the bottom graph the corresponding conductance, i.e. the derivative of the current. The linear dashed curve is the current of the contact in the N/N state. In

![Diagram of conductance and current](image)

**Figure 5.2:** Explanation of conductance minima in the transition region between the S/N and N/N state of the contact.
the S/N state at low voltage, the current is larger in magnitude than the corresponding current in the N/N state due to the Andreev reflection process. As the magnitude of the current increases, the dissipated power and the magnetic field increase, eventually inducing the transition from the S/N to the N/N state. In the transition regions the slope of the current is smaller than that in the other regions leading to the minima in the conductance curve.

The finite-bias minima in the conductance curve of figure 5.2 are a simple example of the signature of the phase transition. In this case the conductance maxima at the energy gap edge, which are the characteristic features of the BTK theory, are preserved since the transition region is located at a bias voltage larger than the superconducting energy gap. The highly anomalous conductance measured by Soulen et al. shown in figure 5.1, can be explained with a transition region that starts already at a bias voltage smaller than the superconducting energy gap (1.5 mV). In other situations the detailed behavior of the current

**Figure 5.3:** Conductance measurements on a series of Pb/Au contacts with different resistance in which above-gap conductance minima are present. The measurements have a vertical offset for clarity and the solid lines are fits of the BTK theory.
in the transition region can be much more complex than presented above, leading to rather exotic conductance curves. When the transition region is smaller, the conductance minima are sharper and may possibly reach negative values, i.e. the current locally decreases with increasing bias [41]. Also the conductance can show multiple minima [43], or the transition region can be wider, which possibly explains observed broad minima extending over several mV [44].

**Point contact series**

A systematic correlation between the position of above-gap conductance minima and the contact resistance is observed in a series of Pb/Au contacts. The contacts are obtained with a single Pb tip and Au sample using the setup with piezoelectric control of the tip movement (see section 4.2). Different contact resistances are obtained by first retracting the tip, breaking the contact, and then lowering the tip again onto the sample at the same spot. Figure 5.3 shows the series sorted by contact resistance. Apart from the sharp above-gap conductance minima, the conductance is in agreement with the BTK theory (solid lines). The energy gap, interfacial scattering strength, and the effective temperature are essentially contact independent, while the position of the conductance minima is systematically correlated with the contact resistance. Figure 5.4 shows the position of the minima as a function of the contact resistance revealing a square root-like dependence.

![Figure 5.4: Position of the conductance minima as a function of the contact resistance. The solid line is a fit of equation (5.8) and the dashed line is a fit of equation (5.9).](image)
Chapter 5. Contact phase transition

5.2 Westbrook-Javan Model

Westbrook and Javan report on a similar observation in a series of Ta/Ag contacts and also found a square root-like dependence of the position of the minima on contact resistance [43]. Here we will perform an analysis similar to theirs.

The magnetic field $H$ generated at the perimeter of the contact by the current $I$ is in approximation given by

$$H = \frac{I}{2\pi a}, \quad (5.1)$$

where $a$ is the contact radius. Since $I$ equals the bias voltage $V$ over the contact resistance $R$, this can be written as

$$H = \frac{V}{2\pi a R}. \quad (5.2)$$

For a specific contact, the voltage $V_c$ at which the phase transition occurs and the critical field $H_c$ are then related by

$$V_c = H_c 2\pi a R. \quad (5.3)$$

In general, when considering a series of contacts such as presented in the previous section, the critical field $H_c$ may vary significantly from contact to contact due to specific geometry and Joule heating differences. In other words, when analyzing a contact series the critical field $H_c$ cannot be regarded as a constant a priori. For the case at hand, however, the dependence of $V_c$ on $R$ is systematic and square root-like. Due to this square root-like dependence the dissipated power at the phase transition $V_c^2/R$ is roughly the same for each contact. In this special case, therefore, it is allowed to assume that for each contact the phase transition occurs at the same effective temperature, and, consequently, that $H_c$ is a constant.

By substituting an appropriate expression that relates the contact radius $a$ with the contact resistance $R$ in equation (5.3), the voltage $V_c$ can be expressed solely in $R$.

Equations for the contact resistance

In general, a good approximation of the resistance of a metallic contact can be obtained using the simple classical equation

$$R \approx \frac{\rho L}{\mathcal{A}}, \quad (5.4)$$

where $\rho$ is the resistivity of the metal and $L$ the length scale of the distance over which the voltage drop occurs. By choosing the appropriate length scale, this equation is applicable to different situations. Trivial is the case of a wire. Here $L$ is simply the length of the wire since the voltage drop occurs over its full length. Less trivial is the case of the contact shown in figure 5.5-(a). Apart from a circular opening, two semi-infinite metals are separated by an infinitely thin insulator. The distance over which the voltage drop occurs depends on the contact radius relative to the mean free path $\ell$ of the electrons.
When the contact radius is small compared to the mean free path \((a \ll \ell)\), the distance over which the voltage drop occurs is roughly \(\ell\), and accordingly

\[
R \approx \frac{\rho \ell}{\pi a^2} \quad \text{(ballistic)}.
\]  

(5.5)

Such a contact is referred to as a ballistic contact. Sharvin derived the exact expression for a ballistic contact with the geometry of figure 5.5-(a) [46]. His expression, known as the Sharvin resistance, is equivalent to the above equation apart from an extra factor \(4/3\).

When the contact radius is large compared to the mean free path \((a \gg \ell)\), the contact is referred to as a diffusive contact. For a diffusive contact the length scale \(L\) is that of \(a\), thus

\[
R \approx \frac{\rho}{\pi a} \quad \text{(diffusive)}.
\]  

(5.6)

The exact equation for a diffusive contact with the geometry shown in figure 5.5-(a) is derived by Maxwell [47]. In his equation the numerical factor in front of the contact radius is 2 instead of \(\pi\).

Equations (5.5) and (5.6) are formally applicable only when the insulator is infinitely thin. Because of this negligible thickness, the only two length scales involved are those of \(a\) and \(\ell\). In practice, however, the insulator has a finite thickness and the contact has the shape of a neck with length \(t\) as shown in figure 5.5-(b). In this case the length scale of the distance over which the voltage drop occurs depends also on this additional dimension. Accordingly, equations (5.5) and (5.6) should be used with great care.

Let us obtain an equation for the neck-shaped contact. When the transport is diffusive, one can assume intuitively that \(L \approx a + t\), which leads to

\[
R \approx \frac{\rho(a + t)}{\pi a^2} \quad \text{(diffusive neck)}.
\]  

(5.7)

Note that when \(t \ll a\) this simplifies to equation (5.6), and when \(t \gg a\) this simplifies to the equation of a wire with length \(t\). Instead of \(a + t\) one can assume that \(L\) is given by \(\sqrt{a^2 + t^2}\). This, however, leads essentially to the same results.

\[
\begin{align*}
\text{Figure 5.5:} & \quad \text{Metallic contact with infinitely thin insulator (a) and with an} \\
& \quad \text{insulator with a finite thickness (b).}
\end{align*}
\]
Chapter 5. Contact phase transition

From the discussion in section 4.2, one expects that the contact resistance is described most appropriately with equation (5.7) since, most likely, the contact has the neck-shape shown in figure 5.5-(b). In this picture, \( t \) can be interpreted as the thickness of the oxide layer.

**Two expressions for \( V_c(R) \)**

With equation (5.7) the contact radius can be expressed in terms of \( R \). This result substituted in (5.3) leads to

\[
V_c = H_c \rho \left( 1 + \sqrt{\frac{4\pi t}{\rho} R + 1} \right),
\]

(5.8)

a dependence on the square root of the resistance. The solid line in figure 5.4 is a best fit of equation (5.8) obtained with \( H_c \rho \approx 0.7 \text{ mV} \) and \( 4\pi t/\rho \approx 0.10 \text{ \( \Omega^{-1} \)} \). If we assume a resistivity \( \rho \) of \( 10^{-7} \text{ \( \Omega/m \)} \), which is typical for a metal, this implies that \( H_c \approx 7 \text{ kA/m} \) and \( t \approx 1 \text{ nm} \).

Instead of using equation (5.7), the resistance of the diffusive neck-shaped contact, we can use equation (5.5), which applies to the neck-less ballistic contact. When this expression is substituted in equation (5.3) one obtains

\[
V_c = H_c 2\sqrt{\frac{\pi \rho \ell}{}} \sqrt{R},
\]

(5.9)

which is also a square root dependence on resistance. The best fit of this equation (dashed line in figure 5.4) is obtained with \( H_c 2\sqrt{\pi \rho \ell} = 0.3 \text{ mV/}\sqrt{\Omega} \), and is in less agreement with the data as compared to the previous one. This fit result gives a critical field of roughly 3 kA/m since for a typical metal the product \( \rho \ell \) is about 1 f\( \Omega \text{m}^2 \).

The deduced thickness \( t \) of about 1 nm seams reasonable for an oxide layer. The obtained critical field \( H_c \) is smaller than 10 kA/m, and therefore significantly smaller than the bulk critical field of Pb, which is 64 kA/m. Westbrook and Javan found a similar difference between their deduced critical field and the bulk critical field of Ta [43]. The superconductor involved in the phase transition of the S/N contacts considered here is not a bulk superconductor but the end of a tip that is in metallic contact with a normal metal. The interaction between the superconductor and the normal metal, and, probably predominantly Joule heating, will suppress the critical field to some extent.

In summary, anomalous conductance minima at finite bias voltage observed for some contacts can be explained by a phase transition of the contact from the S/N state to the N/N state induced by the current-generated field and heating. In a series of contacts it is observed that the bias voltage at which the phase transition occurs, is proportional to the square root of the contact resistance. Consequently, in this series the dissipated power at the phase transition, and therefore the effective temperature, is essentially contact independent. It is shown that simple analysis of such a series can give insight in the microscopic contact geometry.
Chapter 6

Interface spin-flip scattering

The topic of this chapter is the extraction of the polarization from point contacts on ferromagnetic samples. For a given ferromagnet, the extracted polarization shows a considerable contact-to-contact variation. This variation is also reported by another research group and is presently not understood. Here an explanation is given and a quantitative model is presented. First, however, we critically test the modified BTK theory by considering measurements on nonmagnetic samples.

The work described here has been published in Physical Review B [21] and in Journal of Applied Physics [48].

6.1 Test measurements

Since the polarization of the current through nonmagnetic S/N point contacts is known to be zero beforehand, measurements on these contacts can be used to critically test the modified BTK theory. A least-squares procedure converges to the best fit of the modified BTK theory by varying the energy gap $\Delta$, the interfacial scattering strength $Z$, the spin polarization $P$, and the temperature $T$. At first glance, it seems appropriate to fix $T$ at the temperature of the liquid helium bath rather than to use it as a free fitting parameter. However, as will become evident from the test measurements considered here, this will lead to a systematically incorrect extraction of $P$.

Figure 6.1-(a) shows examples of a Nb/Cu and Pb/Al contact immersed in liquid helium at 4.2 K together with least-squares fits (solid lines) performed with $T$ fixed at 4.2 K. Good agreement with the measurement is obtained with unrealistic spin polarizations of 10 and 12%. Figure 6.1-(b) shows the same measurements together with the best model fits obtained when $T$ is used as a free fitting parameter. In this case $P$ typically converges to a value between zero and 1%, and $T$ is systematically about 1 K higher than the experimental temperature. Apparently, in order to extract meaningful polarizations we have to regard $T$ as an effective temperature and use it as a free fitting parameter.

The difference between the effective temperature $T$ and the helium bath temperature can have several causes. First, the temperature of the contact, or, more precisely, the
Figure 6.1: Test measurements performed on a Nb/Cu contact of 100 Ω and a Pb/Al contact of 42 Ω immersed in liquid helium at 4.2 K together with fits of the modified BTK theory (solid lines). In graph (a) the theoretical temperature $T$ is fixed at 4.2 K, while in (b) it is used as a free fitting parameter.

temperature of the Fermi distribution function, can be different from that of the helium bath due to Joule heating and radio-frequent noise. Probably Joule heating is not the main cause since it is observed that $T$ is independent of the contact resistance in a range from $\Omega$’s to kΩ’$s. It is known that pick-up of radio-frequent noise by the wiring connected to a sample induces an elevation of the Fermi distribution temperature. Heating due to radio-frequent noise is found to be especially notorious in transport measurements performed at relatively low bath temperatures of roughly 50 mK provided by dilution refrigerators, and is suppressed by passing the wiring through low-pass filters at low temperatures inside the cryostat [49, 50]. The measurements considered in this thesis are performed only with room temperature low-pass filters present on top of the cryostat.

Second, the temperature of the Fermi distribution function may be equal to that of the helium bath but mechanisms may play a role that have an effect on the conductance
curve similar to that of elevating the Fermi distribution temperature. One mechanism, for example, is the effect of a finite quasi-particle lifetime on the BCS density of states [51, 52]. Another responsible cause might be a gradual variation of \( \Delta \) experienced by the electrons at the interface. The BTK theory assumes that the electrons at the interface experience an abrupt step in \( \Delta \), which is a good approximation for a contact with a radius much smaller than the coherence length of the superconductor [16]. The abrupt step of \( \Delta \) is responsible for the sharp singular-like maximum of the Andreev reflection probability \( A(E) \) at \( E = \Delta \) (see section 3.2). When the contact radius is not much smaller than the coherence length, however, incorporating a gradual variation of \( \Delta \) might become important. Van Son et al. solved the Bogoliubov-de Gennes equation for a gradually varying \( \Delta \) and found that in this case \( A(E) \) has a rounded maximum at \( E = \Delta \) [53].

In summary, a fit of the modified BTK theory leads to meaningful polarizations only when the temperature \( T \) is used as a free fitting parameter. Typically, the fitted temperature is 1 K higher than the helium bath temperature.

6.2 Decay of spin polarization

Values of the spin polarization obtained from a given ferromagnetic sample, generally reveal a large contact-to-contact variation. This is illustrated by the two Pb/Co contacts shown in figure 6.2. The normalized conductance at small bias voltage of the contact with

![Figure 6.2: Conductance of Pb/Co contacts measured at 4.2 K with fits of the modified BTK theory (solid lines). The curves have a vertical offset for clarity.](image-url)
a resistance of 120 Ω, is roughly 1.05, which is smaller than the measured 1.35 for the nonmagnetic contacts of figure 6.1. This suppression of the Andreev reflection conduction process is caused by the spin polarization. The extracted polarization for this Pb/Co contact is 40 %. The contact with a resistance of 1.9 kΩ, however, gives a polarization of only 8 %. This small polarization is directly visible from the higher conductance maxima.

The interfacial scattering strength $Z$ extracted from the two measurements are considerably different. When the polarization extracted from numerous contacts is plotted as a function $Z$, as is done in figure 6.3 for Co, a systematic decrease with $Z$ becomes apparent. Apart from the considerable scatter in the data, the correlation is universal as it is obtained from bulk as well as thin film Co samples with both Pb and Nb tips. There is no observable correlation between $P$ and contact resistance, implying that the $Z$-value alone is decisive for the magnitude of $P$.

A similar decrease of $P$ with $Z$ is reported by others for contacts on Co, Fe and Ni [20], half-metallic CrO$_2$ [15], and La$_x$Sr$_{1-x}$MnO$_3$ (LSMO) [24]. Currently the decay of $P$ with $Z$ is not understood and no quantitative model is available to explain the data. To extract the “true” value of the spin polarization, an empirical polynomial of second order in $Z$ is

![Figure 6.3: Polarization from numerous Pb/Co and Nb/Co contacts plotted as a function of $Z$ revealing a systematic decrease with the interfacial scattering strength $Z$. The solid line is a fit of an empirical second order polynomial to the data with $Z \leq 0.5$.](image)
Figure 6.4: Polarization plotted as a function of $Z^2$ for Co, Fe and Gd (open symbols). For comparison data of Co, Fe (taken from ref. [20]), CrO$_2$ and La$_x$Sr$_{1-x}$MnO$_3$ (taken from ref. [15] and [24] resp.) are included (black symbols). The solid lines are fits of an exponential decay.
fitted to the data and an extrapolation of $P$ towards zero $Z$ is used. Figure 6.3 shows that a good fit with a second order polynomial is obtained only when one disregards the data with $Z > 0.5$. The remainder of this chapter presents a quantitative explanation of the decrease of $P$ with $Z$.

The interfacial scattering strength $Z$ is an abstract mathematical parameter, the strength of a delta-function, without direct physical meaning. In order to understand the experimental results, $Z$ must be identified with parameters which have a direct physical meaning. A first important hint is given by equation (3.18),

$$\text{transmission} = \frac{1}{1 + Z^2},$$

which is the equation for the transmission of electrons incident on a delta-function scattering potential. The transmission depends explicitly on $Z^2$, which makes it independent of the sign of $Z$. This indicates that $Z^2$ is the appropriate scattering parameter with a direct physical meaning rather than $Z$. Consequently, the polarization should not be plotted as a function of $Z$, but as a function of $Z^2$. Figure 6.4 shows the polarization obtained from various ferromagnetic samples as a function of $Z^2$. Included are the Co data of figure 6.3, the data obtained from Fe and Gd samples, and the data published by others [15, 20, 24] (black symbols). Plotted in this way, one observes an exponential decay of the polarization over the full range of $Z^2$. A quantitative model which explains the exponential decay is described below.

### 6.3 Interface spin-flip scattering

In order to understand the experimental results, we must identify the main scattering mechanism contributing to $Z^2$. Three potential contributions can be distinguished: scattering due to the mismatch of the electronic band structures at the interface, specular reflection at a tunnel barrier, and scattering at impurities and lattice defects. The first contribution to $Z^2$ is intrinsic since it is present in a perfectly clean contact without defects. Based on a free-electron approximation [42] it can be estimated that this contribution has an order of magnitude of $10^{-2}$. An ab-initio calculation [54], fully accounting for the transition metal band structure, results in an intrinsic mismatch contribution of roughly $10^{-1}$. These numbers are small compared to the measured values of $Z^2$, suggesting that the intrinsic mismatch plays a relatively unimportant role in the contacts. A typical tunnel barrier is equivalent to a delta-potential barrier with a large $Z$, much larger than the measured values. Therefore we consider the presence of a tunnel barrier at the interface as unlikely and assume that mostly impurity scattering and scattering at lattice defects contributes to $Z^2$.

By modelling this type of interface scattering with the use of a delta-potential, as is done in the BTK theory, one is assuming a picture as shown in figure 6.5-(a), where an incident electron is reflected or transmitted involving *at most a single scattering event*. In practice, however, an electron may be transmitted or reflected through *multiple scattering events* in
both forward and backward direction as shown in figure 6.5-(b). Thus, the measured value of $Z^2$ should be considered as an “effective” scattering parameter which measures multiple scattering events occurring in an extended interface region.

A quantitative expression for $Z^2$ can be obtained by calculating the transmission $T$ of electrons through a scattering region of width $\ell$. We consider an electron travelling in $x$-direction only, which enters the scattering region at $x = 0$ and is transmitted when it reaches $x = \ell$. Within a distance $dx$ the scattering probability is $dx/\lambda$, where $\lambda$ is the electron mean free path. At a particular scattering site, the electron can be scattered while it maintains its direction of travelling, i.e. it can scatter in forward direction, or it can be backward reflected. We assume that it is $\psi$ times more likely for the electron to be scattered in forward direction. A differential equation for $T(x)$ can be deduced by calculating $T(x+dx)$ from $T(x)$ by considering all possibilities for transmission through $dx$ and adding their probabilities. The transmission probability through $dx$ without scattering is

$$1 - \frac{dx}{\lambda}.$$  

The probability for transmission accompanied by one forward scattering event is

$$\frac{dx}{\lambda} \left( \frac{\psi}{1+\psi} \right),$$

and the probability for transmission via two backscattering events is

$$\frac{dx}{\lambda} \left( \frac{1}{1+\psi} \right) (1 - T(x)), $$

etc. Summarizing all these probabilities leads to

$$\frac{dT}{dx} = -\frac{1}{\lambda(1+\psi)} T^2,$$  

(6.1)
with the solution at $x = \ell$

$$T = \frac{1}{1 + \frac{1}{1 + \psi} \frac{\ell}{\lambda}}. \quad (6.2)$$

Expressions that relate the transmission with parameters such as $\ell/\lambda$ have been derived earlier with a different approach (see for example ref. [55]). Interestingly, equation (6.2) has the same form as equation (3.18),

$$T = \frac{1}{1 + Z^2},$$

which gives the transmission of electrons incident on a delta-function scattering potential. This similarity suggests that we can write

$$Z^2 = \frac{1}{1 + \psi} \frac{\ell}{\lambda}. \quad (6.3)$$

The quantity $Z^2$ scales with $\ell/\lambda$, which is a measure for the average number of scattering events of a transmitted electron. When the electrons scatter mostly in forward direction $\psi$ is large and $Z^2$ is small. In the fully backward scattering limit $\psi$ is zero and $Z^2 = \ell/\lambda$.

The spin polarization of electrons travelling through the scattering region will decrease when a spin-flip probability $\alpha$ exists for each scattering event. For a given spin polarization of the incident electrons $P_0$, the transmitted spin polarization $P$ and reflected spin polarization $Q$ can be calculated. A system of two differential equations for $P$ and $Q$ can be deduced in a similar approach as is done for obtaining equation (6.1). This system can be formulated in the compact form

$$\frac{dQ}{d\zeta} = 1 - 2\rho Q + Q^2 \quad \text{and} \quad \frac{dP}{d\zeta} = (Q - \rho)P, \quad (6.4)$$

by using the quantities $P = TP$ and $Q = (1 - T)Q$. The parameter $\rho$ is defined by $\rho = (1 + 2\alpha\psi)/(1 - 2\alpha)$ and $\zeta$ is defined by $\zeta = (1 - 2\alpha)Z^2$. Equation (6.5) can be solved to find $P$ when $Q$ is known from equation (6.4). However, in the case of dominant forward scattering (large $\psi$), $Q$ can be neglected in equation (6.5) and the approximate solution for $P$ is

$$P \approx P_0 \exp(-2\alpha\psi Z^2) \quad \text{(dominant forward scattering)}. \quad (6.6)$$

For arbitrary $\psi$ the solutions are

$$P = P_0 \frac{(1 + Z^2)\eta}{(1 + 2\alpha\psi) \sinh(\eta Z^2) + \eta \cosh(\eta Z^2)} \quad \text{and} \quad (6.7)$$

$$Q = P_0 \frac{1 + Z^2}{Z^2} \frac{(1 - 2\alpha) \sinh(\eta Z^2)}{(1 + 2\alpha\psi) \sinh(\eta Z^2) + \eta \cosh(\eta Z^2)}, \quad (6.8)$$

64
where $\eta^2 = 4\alpha(1+\psi)+4\alpha^2(\psi^2-1)$. Figure 6.6 shows $P/P_0$ calculated with equation (6.7) for the backward scattering regime ($\psi = 0$) and for dominant forward scattering ($\psi = 100$). For a given value of $Z^2$ the transmitted polarization is higher in the backward scattering regime since in this regime the transmitted electrons have experienced less scattering events.

The width $\ell$ in equation (6.3) relates to the characteristic dimension of the region where the Andreev reflection process occurs. Since this is an extended region, the measured $P$ is not necessarily the polarization of the electrons at $x = \ell$ alone. As a consequence, the simple interface spin-flip scattering model, which calculates the $P$ for electrons at $x = \ell$ alone, is strictly not correct and should be extended by considering weighted contributions of $P$'s at different positions. Nevertheless, the results derived here capture the essential physics involved.

The dependence on $Z^2$ in the dominant forward scattering regime is similar to what is observed in the experiment. The solid lines in figure 6.4 are fits of equation (6.6) with the parameters $P_0$ and $\alpha\psi$ as listed in table 6.1. The extracted $P_0$ thus represents the spin polarization of the ferromagnetic sample measured with Andreev reflection spectroscopy.

The considerable noise in the data of figure 6.4 is not due to a poor accuracy of the fitting procedure. The noise reflects the coarse experimental approach used to obtain the contacts. As explained in section 4.2, the exposure of tip and sample to air prior to
Table 6.1: Fit results (see text for details).

<table>
<thead>
<tr>
<th>Material</th>
<th>$P_0$ [%]</th>
<th>$\alpha\psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>47 ± 2</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>46 ± 3</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>Gd</td>
<td>45 ± 4</td>
<td>2.1 ± 0.3</td>
</tr>
<tr>
<td>CrO$_2$[15]</td>
<td>96 ± 2</td>
<td>0.16 ± 0.03</td>
</tr>
<tr>
<td>La$<em>x$Sr$</em>{1-x}$MnO$_3$[24]</td>
<td>80 ± 1</td>
<td>0.27 ± 0.01</td>
</tr>
</tbody>
</table>

the formation of the contact leads to a poorly defined interface. With use of a cleaner experimental approach, possibly the decay of $P$ with $Z^2$ can be studied more accurately, potentially enabling a quantitative experimental study of spin-flip scattering.

Due to the poor definition of the contacts it is difficult to unambiguously identify and localize the scattering contributions to $Z^2$ and responsible spin-flip mechanisms. Nevertheless, one may speculate on the mechanisms involved based on the experimental observations. The width $\ell$ in equation (6.3) is related to the characteristic dimension of the region where Andreev reflection occurs. If the majority of the electrons are Andreev reflected in the proximity region in S, within a superconducting coherence length from the interface, then spin-flip scattering occurs due to the spin-orbit interaction in the superconductor [56, 57]. The spin-orbit interaction in Pb is at least one order of magnitude larger than in Nb. The independence of the observed polarization decay on the choice between Pb or Nb as the superconducting tip, therefore, indicates that the spin-orbit interaction in the superconductor is not important. A more important contribution might be spin-flip due to the interaction between the electron magnetic moment and atomic magnetic moments in an atomically intermixed interface region. This picture seems reasonable in view of the used contacting procedure.

Finally, it is apparent from figure 6.4 that the polarization measured on CrO$_2$ and La$_x$Sr$_{1-x}$MnO$_3$ (LSMO) [15, 24] shows a significantly weaker decay as compared to Co, Fe and Gd. This difference can be explained by the mechanical properties of the samples. The atomic bonds in the ionic CrO$_2$ and LSMO crystals are much stronger as compared to the metal bonds in the Co, Fe and Gd samples. Most likely, this leads to a different interface structure with less atomic intermixing.

In summary, the extracted spin polarization systematically decays with the interfacial scattering strength $Z$. It is argued that $Z^2$ is the appropriate physical scattering parameter rather than $Z$. When plotted as a function of $Z^2$, the spin polarization shows an exponential decay. This exponential decay is explained with a simple model involving spin-flip scattering in an extended interface region.
Part II

Tunnel junctions
Chapter 7

Introduction to spin-polarized tunneling

This chapter introduces the spin-polarized tunneling technique and gives a brief review of its history. The quantitative theory is described in chapter 8.

7.1 Normal metal-superconductor tunneling

The spin-polarized tunneling technique involves the measurement of the current-voltage relation of a tunnel junction consisting of a normal metal and a superconducting electrode in presence of a magnetic field as shown in figure 7.1. We will introduce the technique by first considering tunneling in absence of the field, and thereafter consider what happens when the field is applied.

The energy diagram of the superconductor shows an energy gap $\Delta$ between the level of the Cooper pairs and the single-electron states. This energy gap is the minimum energy needed per electron to break a Cooper pair, and is responsible for the characteristic shape

![Figure 7.1: Illustration of the spin-polarized tunneling technique.](image-url)
Figure 7.2: Energy diagram of a normal metal/superconductor tunnel junction in case of different bias voltages (a, b, and c), and the current-voltage relation of the junction (d).
of the current-voltage relation. The bias voltage dependence of the tunnel current can be understood qualitatively from the energy diagrams shown in figure 7.2. At zero bias (a), the Fermi level of the superconductor, i.e. the energy level of the Cooper pairs, is lined up with that of the normal metal. We know from the previous part of this thesis that in absence of a tunnel barrier, transport between the normal metal and the superconductor is possible via the Andreev reflection process. In this process two electrons with opposite spin simultaneously enter the condensate of the Cooper pairs. In theory, this process is also possible when a tunnel barrier is present, however, since it requires simultaneous tunneling of two electrons, its probability to occur is negligible as compared to single-electron tunneling processes (see section 3.2).

For the description of the current-voltage relation, we assume that a positive bias lowers the energy of the superconductor with respect to the normal metal. When \( eV \) is smaller than \( \Delta \), the electrons in the normal metal are not able to tunnel into the superconductor since no single-electron states are available. The tunnel current starts to flow only after \( eV \) is increased to \( \Delta \) as shown in diagram (b). At this bias, the electrons in the normal metal have access to the empty single-electron states in the superconductor. When the bias is increased further, more and more electrons below the Fermi level in the normal metal tunnel into the empty states in the superconductor causing the current to increase.

At negative bias, the energy of the superconductor is raised with respect to the normal metal. Since the energy level of the Cooper pairs is located above the Fermi level of the normal metal, empty states in the normal metal are available for the paired electrons to tunnel into. However, at small negative bias the current remains zero since, as mentioned previously, simultaneous tunneling of the two electrons of a Cooper pair is an extremely unlikely process. The current starts to flow at a bias \( eV = -\Delta \) due to the onset of the tunnel process shown in figure 7.2-(c). In this process one electron of a Cooper pair tunnels into the normal metal releasing an energy \( \Delta \) which is used to bring the other electron into a single-electron state in the superconductor. The number of pairs that split up in this way increases with the magnitude of the bias voltage since at larger bias a larger energy window with single-electron states in the superconductor and normal metal is available.

The current-voltage relation of the tunnel junction is shown in figure 7.2-(d). The bias at which the current starts to flow thus marks the superconducting energy gap. The dashed line corresponds to the current measured when the superconductor is in the normal state. When the magnitude of the bias is increased to values much larger than \( \Delta \), the current approaches to the normal state current since the influence of the gap on the tunnel current becomes negligible.

### 7.2 Conductance and density of states

In any tunneling experiment it is common to work with conductance, i.e. the derivative of the current-voltage relation, since the conductance gives direct information of the parameter of interest, namely the density of states of the electrodes. Figure 7.3 shows the current-voltage together with the conductance-voltage relation.
Figure 7.3: The current-voltage and conductance voltage relation of a N/S tunnel junction. The conductance is the derivative of the current. At zero temperature (dashed lines) the conductance is directly proportional to the density of states of the superconductor.

So far, we have explained the current-voltage relation of the tunnel junction by using the energy diagram of the superconductor and did not talk about density of states. We can explain the current-voltage relation of the tunnel junction alternatively, by assigning a single-electron density of states to the superconductor.

As argued in section 1.2, the tunnel current between two electrodes, and therefore also the conductance, is proportional to the product of their density of states at the Fermi level, a result which will be formally derived in chapter 8. The energy scale in figure 7.3 is determined by $\Delta$, which is for most superconductors about 1 meV. Since the density
of states of a normal metal typically shows variation on an energy scale of eV’s, it is essentially constant on the meV scale. Consequently, the conductance reflects exclusively the shape of the single-electron density of states of the superconductor. Apparently, this density of states contains an energy gap with a width of $2\Delta$ centered at the Fermi level and maxima at the edges of the energy gap. Generally, the sharpness of the maxima is determined by the temperature and is roughly equal to a few times $k_B T$, which is the thermal broadening of the Fermi level. At zero temperature (dashed lines), the conductance is directly proportional to the density of states.

The explanation of the current-voltage relation using a single-electron density of states for the superconductor is shown in figure 7.4. Here the superconductor is equivalent to a semiconductor with a valence band filled with single electrons and an empty conduction band. At zero bias (a) the gap $2\Delta$ is centered at the Fermi level. At $eV = \Delta$, current starts to flow as empty states in the conduction band of the superconductor become accessible for the electrons in the normal metal (b). At $eV = -\Delta$, current starts to flow in the other direction as the electrons in the valence band of the superconductor tunnel into the empty states at the Fermi level of the normal metal (c).

The spin-polarized tunneling technique makes use of a superconducting electrode solely because the single-electron density of states of the superconductor has a suitable shape. In other words, theoretically one could perform the spin-polarized tunneling experiment also using a semiconducting electrode with a density of states equivalent to that of the superconductor. From hereon we will adopt the semiconductor representation.
7.3 The effect of an applied magnetic field

The density of states reflected by the conductance measurement is the sum of the density of spin-up states and the density of spin-down states. In absence of a magnetic field, no energy is required to flip the spin of an electron, and, accordingly, the spin-up and spin-down density of states coincide. This situation changes when a magnetic field is applied parallel to the plane of the tunnel junction. The magnetic field penetrates the superconductor uniformly since the thickness of the superconducting electrode is much smaller than the penetration depth of the magnetic field. In presence of the field, an energy is required to rotate the spin of an electron against the field direction. When the field points in upward direction and has a magnitude \( B \), the energy required to change a spin-up electron into a spin-down electron is \( 2\mu_B B \), where \( \mu_B \) is the magnetic moment of the electron. In other words, the magnetic field lowers the energy of the spin-up electrons and raises the energy of the spin-down electrons. This energy difference is known as Zeeman splitting. Consequently, the magnetic field shifts the density of spin-up states to lower energy and the density of spin-down states to higher energy. Figure 7.5-(a) shows how these energy shifts lead to four maxima in the conductance. The maxima are clearly resolved when the Zeeman splitting \( 2\mu_B B \) is large as compared to \( k_B T \), the sharpness of the maxima. The maximum applicable field is limited by the critical field \( B_c \) of the superconducting electrode. Critical fields larger than 4 Tesla can be obtained with aluminum superconducting electrodes, and, typically, fields of 2 to 3 Tesla are applied. With \( \mu_B \approx 58 \mu eV/T \) and \( k_B \approx 86 \mu eV/K \) one finds then that a temperature below 1 K is required to clearly resolve the Zeeman splitting.

The two conductance maxima at low bias, those numbered 1 and 2 in figure 7.5-(a), give a direct indication of the spin polarization of the tunneling electrons. Since at the position of maximum 1 the density of spin-up states is zero, maximum 1 is a direct measure of the spin-down conductance. Likewise, maximum 2 is a direct measure of the spin-up conductance. Apparently, in the example of figure 7.5-(a) the spin-up and spin-down conductance are equal, i.e. the tunneling spin polarization is zero.

When there are more spin-up electrons tunneling than spin-down electrons, maximum 2 is larger than 1 as shown in figure 7.5-(b). In this particular example the polarization is 40 % and positive since the magnetization of the normal metal is aligned with the magnetic field in upward direction, i.e. tunneling is dominated by majority electrons. To a good approximation, the polarization \( P \) is given by the relative difference between the height of maxima 2 and 1,

\[
P \approx \frac{G_2 - G_1}{G_2 + G_1},
\]

indicated by the arrow in the figure. A most accurate extraction of the polarization is obtained by fitting a model (described in the next chapter) to the measured conductance curve.

The title of the bias voltage axis in figure 7.5 reads \( V_S - V_N \). This is conform the convention that the bias voltage is applied to the junction with the normal electrode connected to ground. Note that when the direction of the magnetic field is reversed,
Figure 7.5: Conductance of a S/N tunnel junction in which the spin-up and spin-down density of states in the superconductor are Zeeman split by a magnetic field $B$. The polarization of the tunneling electrons is zero in (a), +40 % in (b), and -80 % in (c). The thin dashed and solid line in graph (a) represent the individual spin-up and spin-down density of states, respectively.
the conductance-voltage curve is the same since the magnetization direction of the normal electrode is also reversed. In this situation, however, maximum 2 corresponds to spin-down electrons and maximum 1 to spin-up electrons.

To end the introduction of the spin-polarized tunneling technique, we consider the case of negative polarization as shown in figure 7.5-(c). Here maximum 1 is larger than 2, which means that the tunnel current is dominated by spin-down electrons. These electrons are the minority electrons since the magnetization of the normal metal is aligned with the field in upward direction.

7.4 Brief history

Here we put the results presented later in this thesis in perspective by briefly reviewing earlier work on spin-polarized tunneling. An extensive, but somewhat dated review is published by Tedrow and Meservey [58].

The superconductor used in the tunnel junctions for spin-polarized tunneling measurements is usually aluminum. There are two reasons responsible for this important role of aluminum. First, aluminum is a superconductor with a low atomic number. As will be explained in section 8.3, clear observation of the Zeeman split spin-up and spin-down superconducting density of states is possible only when the spin-orbit scattering rate in the superconductor is low and thus requires a low atomic number. Consequently, common superconductors such as niobium, lead and tantalum are not suitable and only a few superconductors other than aluminum can be used. For example, clear Zeeman splitting is demonstrated with vanadium and titanium-vanadium alloys. Since the atomic numbers in the recently discovered high \( T_c \) superconductor MgB\(_2\) are low [59], Zeeman splitting should be clearly observable also with this superconductor. This, however, is still to be demonstrated experimentally.

The second reason for the almost exclusive role of aluminum in spin-polarized tunneling is the defect and pinhole-free amorphous AlO\(_x\) tunnel barrier obtained by exposing metallic aluminum to oxygen. Consequently, most published work is based on Al/AlO\(_x\)/N tunnel junctions obtained by oxidation of the top part of an aluminum electrode followed by the deposition of the normal metal on top of the AlO\(_x\) barrier. Preparation of such junctions seems rather straightforward, however, as will become clear in chapter 10, obtaining aluminum electrodes with sufficiently high critical fields is far from trivial.

Zeeman splitting in the conductance of Al/AlO\(_x\)/N tunnel junctions was observed for the first time by Tedrow and Meservey in the early 70’s. Soon thereafter values of the tunneling polarization in junctions with various top electrodes were obtained. These early polarizations were determined simply from the differences in the conductance maxima using a procedure similar to that explained in the previous section. This procedure, however, leads to a small but significant underestimation of the polarization since it does not take into account the effect of a finite spin-orbit scattering rate on the spin-up and spin-down superconducting density of states. This effect will be explained in more detail in section 8.3. When the importance of spin-orbit scattering was recognized, the early values of the po-
larization were corrected. These corrected results are listed in table 7.1. This table gives an overview of the polarizations measured with the spin-polarized tunneling technique.

The tunneling polarization in Al/AlO₅/N junctions with Co, Fe, and Ni top electrodes, ranges from +30 to +45 %. In section 1.2 we have considered the spin polarization of the bulk density of states in Co, Fe, and Ni, which was simply the relative difference in the spin-up and spin-down density of states at the Fermi level obtained from first principle calculations for bulk crystals (equation (1.5)). This polarization is negative in Co and Ni in contrast to the positive tunneling spin polarization. In the early years of spin-polarized tunneling, several theoretical models were proposed to explain the difference between the tunneling polarization and the calculated polarization of the density of states [58]. These models, however, assume that the tunneling polarization is determined exclusively by the band structure of the ferromagnetic electrode. Recent TMR experiments and calculations have indicated that the tunneling polarization is not exclusively determined by the bulk electronic structure of the ferromagnet, but instead by the electronic structure of the ferromagnet/barrier interface and the material used for the tunnel barrier [70–72]. The barrier dependence of tunneling spin polarization is the topic of chapter 11.

Table 7.1: Tunneling spin polarization values obtained with the spin-polarized tunneling technique. The asterisk (∗) indicates a crystalline electrode or barrier.

<table>
<thead>
<tr>
<th>junction</th>
<th>P [%]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/AlOₓ/Ni</td>
<td>32-46</td>
<td>Moodera[60, 61], Parkin [62]</td>
</tr>
<tr>
<td>Al/AlOₓ/Co</td>
<td>40 ± 2</td>
<td>Moodera[60], Parkin [62], Kant [63]</td>
</tr>
<tr>
<td>Al/AlOₓ/Fe</td>
<td>42 ± 2</td>
<td>Moodera[60], Parkin [62], Kant [63]</td>
</tr>
<tr>
<td>Al/AlOₓ/Co₈₄Fe₁₆</td>
<td>53 ± 2</td>
<td>Moodera[60], Parkin [62]</td>
</tr>
<tr>
<td>Al/AlOₓ/Ni₄₀Fe₆₀</td>
<td>55 ± 2</td>
<td>Parkin [62]</td>
</tr>
<tr>
<td>Al/AlOₓ/MnSb</td>
<td>31 ± 2</td>
<td>Parkin [64]</td>
</tr>
<tr>
<td>Al/AlOₓ/Gd</td>
<td>13 ± 4</td>
<td>Meservey and Tedrow [65]</td>
</tr>
<tr>
<td>Al/AlOₓ/Tb</td>
<td>5 ± 2</td>
<td>Meservey and Tedrow [65]</td>
</tr>
<tr>
<td>Al/AlOₓ/Dy</td>
<td>6 ± 2</td>
<td>Meservey and Tedrow [65]</td>
</tr>
<tr>
<td>Al/AlOₓ/Ho</td>
<td>6 ± 2</td>
<td>Meservey and Tedrow [65]</td>
</tr>
<tr>
<td>Al/AlOₓ/Er</td>
<td>5 ± 2</td>
<td>Meservey and Tedrow [65]</td>
</tr>
<tr>
<td>Al/AlOₓ/Tm</td>
<td>3 ± 2</td>
<td>Meservey and Tedrow [65]</td>
</tr>
<tr>
<td>NiMnSb*/AlOₓ/Al</td>
<td>28 ± 2</td>
<td>Moodera [66]</td>
</tr>
<tr>
<td>Ni*/AlOₓ/Al</td>
<td>25 ± 2</td>
<td>Moodera [61]</td>
</tr>
<tr>
<td>La₀.⁶⁷Sr₀.₃₃MnO₅ /SrTiO₃/Al</td>
<td>78 ± 1</td>
<td>Worledge [67]</td>
</tr>
<tr>
<td>SrRuO₃ /SrTiO₃/Al</td>
<td>-10 ± 1</td>
<td>Worledge [68]</td>
</tr>
<tr>
<td>CrO₂ /Cr₂O₃/Al</td>
<td>100</td>
<td>Parker [69]</td>
</tr>
<tr>
<td>Al/MgO/Co</td>
<td>30 ± 2</td>
<td>Kant [63]</td>
</tr>
<tr>
<td>Al/MgO/Fe</td>
<td>30 ± 2</td>
<td>Kant [63]</td>
</tr>
</tbody>
</table>

77
In the 90’s the high application potential of the TMR effect in magnetic tunnel junctions triggered a renewed interest in the spin-polarized tunneling technique. As a result, the polarization in Al/AlO$_x$/N junctions with a large variety in the in 3$d$ metal alloy composition were measured [62]. In addition to these alloys, more complex crystalline ferromagnetic electrodes were studied. A unique tunneling polarization is measured in SrRuO$_3$/SrTiO$_3$/Al junctions [68], namely -10 %. To date, this is the only reported negative polarization measured with the spin-polarized tunneling technique.

For other complex crystalline materials, calculations predict a half-metallic band-structure (see section 1.2). Half-metals are of interest since they may potentially lead to a high tunneling polarization and, accordingly, to high TMR effects. To date, the half-metals used in junctions for spin-polarized tunneling measurements are NiMnSb and CrO$_2$. The tunneling polarization measured in NiMnSb/AlO$_x$/Al junctions is 28 % [66]. This relatively low polarization is in sharp contrast with the calculated bulk density of states polarization and reflects the decisive role of the ferromagnet/barrier interface. Recently, Parker et al. have measured 100 % tunneling polarization in a CrO$_2$/Cr$_2$O$_3$/Al junction [69].

Another new aspect explored with the spin-polarized tunneling technique is the thermal stability of the polarization. This aspect, technologically relevant for the development of MRAM, is the topic of chapter 12.
Chapter 8

Theory of spin-polarized tunneling

In the previous chapter the spin-polarized tunneling technique is introduced. This chapter describes the theory which is used to extract the tunneling polarization from the measurement.

8.1 Conductance and the BCS density of states

Here we derive an exact equation for the normalized conductance of a normal metal/superconductor (N/S) tunnel junction. The number of electrons, which tunnel from one electrode into the other at a specific energy, is proportional to the product of the number of electrons present in the source electrode, the tunnel probability $T$, and the number of empty states present in the other electrode,

$$\text{tunnel current } \propto (\text{number of electrons}) \times T \times (\text{number of empty states}). \tag{8.1}$$

The number of electrons is given by the density of states multiplied by the probability to find an occupied state. This probability is given by the Fermi distribution function $f(E)$. The number of empty states is given by the density of states multiplied by the probability to find an empty state, which is $1 - f(E)$. When $\sigma(E)$ is the density of states in N and $\rho_s(E)$ the density of states in S, the current at energy $E$ flowing from N to S at zero bias is proportional to

$$\sigma(E)f(E) \times T(E) \times \rho_s(E)[1 - f(E)], \tag{8.2}$$

and the current flowing from S to N is proportional to

$$\sigma(E)[1 - f(E)] \times T(E) \times \rho_s(E)f(E). \tag{8.3}$$

We assume for convenience that a positive bias voltage $V$ raises the energy of N with respect to S. This means that in N we have to replace $E$ by $E - eV$. Thus, in presence of a bias voltage the current from N to S becomes

$$\sigma(E - eV)f(E - eV) \times T(E) \times \rho_s(E)[1 - f(E)], \tag{8.4}$$
and the current from $S$ to $N$

$$\sigma(E - eV)[1 - f(E - eV)] \mathbb{T}(E) \rho_s(E)f(E). \tag{8.5}$$

The net current at energy $E$ is proportional to the difference of these expressions. This difference can be simplified to

$$\sigma(E - eV)\mathbb{T}(E)\rho_s(E)[f(E - eV) - f(E)]. \tag{8.6}$$

The total current $I$ is obtained by integrating this result over all energies:

$$I \propto \int \sigma(E - eV)\mathbb{T}(E)\rho_s(E)[f(E - eV) - f(E)] \, dE. \tag{8.7}$$

The function $[f(E - eV) - f(E)]$ is zero everywhere except for a region with a magnitude $eV$ near the Fermi level. On the voltage scale of interest, which is negligible as compared to the Fermi energy and the tunnel barrier height, the density of states in $N$ and the tunnel probability can be regarded as a constant so that they can be moved in front of the integral,

$$I \propto \sigma \mathbb{T} \int \rho_s(E)[f(E - eV) - f(E)] \, dE. \tag{8.8}$$

For the conductance $G_{NS} = dI/dV$ we can write

$$G_{NS} \propto -e \sigma \mathbb{T} \int \rho_s(E)f'(E - eV) \, dE, \tag{8.9}$$

where $f'$ is the derivative of the Fermi distribution function. The function $-f'(E)$ is similar to a delta-function. It is zero everywhere except near $E = 0$ where it has a pulse-shape with a width proportional to $k_B T$. At zero temperature the integral in the above expression is equal to $\rho_s(eV)$ by which $G_{NS}$ simplifies to

$$G_{NS} \propto e \sigma \mathbb{T} \rho_s(eV) \quad \text{(zero temperature).} \tag{8.10}$$

Apparently, the conductance is a measure of the product of the normal metal and the superconducting density of states. Since $\sigma$ is essentially a constant on the energy scale of interest, the conductance thus directly reflects the shape of the superconducting density of states. To obtain the conductance $G_{NN}$ of the junction in the normal state, we replace $\rho_s$ by $\rho_N$ in expression (8.9). Like $\sigma$, the normal state density of states $\rho_N$ can be regarded as constant and it can be moved in front of the integral. Since the integral of the function $-f'(E)$ equals one we obtain

$$G_{NN} \propto e \sigma \mathbb{T} \rho_N. \tag{8.11}$$

The ratio between $G_{NS}$ and $G_{NN}$, referred to as the normalized conductance, becomes

$$\frac{G_{NS}}{G_{NN}} = -\int \frac{\rho_s}{\rho_N} f'(E - eV) \, dE. \tag{8.12}$$
The normalized conductance is a convolution of $\rho_S/\rho_N$ and the function $-f'(E)$. Note that we have derived this equation earlier in section 3.2 as a special result of the BTK theory. An expression for $\rho_S/\rho_N$ is introduced in section 3.1. This expression is known as the Bardeen Cooper Schrieffer (BCS) density of states. Here we will write it as

$$\frac{\rho_S}{\rho_N} = \sgn(E) \Re \left( \frac{z}{\sqrt{z^2 - 1}} \right),$$

(8.13)

where $z = E/\Delta$.

A description of the conductance in case of an applied magnetic field requires a modified BCS density of states which includes the Zeeman splitting in the spin-up and spin-down electron energies. This modified BCS density of states is described in the next section. We end this section with some remarks on how to measure the normalized conductance in an experiment. Formally, the normalized conductance should be obtained by normalizing the conductance measured below the transition temperature $T_c$ with the normal state conductance measured above $T_c$. This is most useful when the normal state conductance shows a considerable dependence on bias voltage. Usually, however, the normal state conductance is constant and its measurement is not necessary. In this case the normalized conductance is obtained simply by normalizing the conductance by its value at large bias voltage.

### 8.2 Zeeman splitting and spin polarization

Next we consider a magnetic field with magnitude $B$ applied parallel to the plane of the tunnel junction. When the thickness of the superconducting electrode is small as compared to the penetration depth of the magnetic field, the field penetrates the superconductor uniformly. Due to the interaction between the electron magnetic moment $\mu_B$ and the field, the electron energy depends on its spin direction. When the field points in upward direction, the energy of the spin-up electrons is lowered by $\mu_BB$ and the energy of the spin-down electrons is raised by $\mu_BB$. This energy difference, known as Zeeman splitting, can be incorporated by splitting $\rho_S/\rho_N$ into a spin-up and spin-down part

$$\frac{\rho_S}{\rho_N} = \frac{\rho^\uparrow_S}{\rho_N} + \frac{\rho^\downarrow_S}{\rho_N},$$

(8.14)

and by replacing $E$ with $E - \mu_BB$ and $E + \mu_BB$ in the spin-up and spin-down part respectively. In analogy with equation (8.13) this leads to

$$\frac{\rho^\uparrow_S}{\rho_N} = \frac{1}{2} \sgn(E - \mu_BB) \Re \left( \frac{u}{\sqrt{u^2 - 1}} \right),$$

(8.15)

$$\frac{\rho^\downarrow_S}{\rho_N} = \frac{1}{2} \sgn(E + \mu_BB) \Re \left( \frac{d}{\sqrt{d^2 - 1}} \right),$$

(8.16)
where $u$ and $d$ are defined by
\[
\begin{align*}
    u &= \frac{E - \mu_B B}{\Delta} \\
    d &= \frac{E + \mu_B B}{\Delta}.
\end{align*}
\]

The substitution of equation (8.14) into (8.12) leads to
\[
\frac{G_{NS}}{G_{NN}} = \left( \frac{G_{NS}}{G_{NN}} \right) \uparrow + \left( \frac{G_{NS}}{G_{NN}} \right) \downarrow \tag{8.19}
\]
(zero polarization),

where
\[
\left( \frac{G_{NS}}{G_{NN}} \right) \uparrow = - \int \frac{\rho_S}{\rho_S} f'(E - eV) \, dE. \tag{8.20}
\]

Equation (8.19) needs to be modified to account for spin polarization. In the modified equation the spin-up and spin-down conductance are weighted differently in accordance to the spin polarization. To find the appropriate weighting factors we derive an expression for the conductance based on the general definition of spin polarization (equation (1.1)). The polarization is defined as the relative difference in the spin-up and the spin-down current. Equivalently, the polarization can be defined as the relative difference in the spin-up and spin-down conductance,
\[
P = \frac{G' - G'}{G}, \tag{8.21}
\]
where
\[
G = G' + G'. \tag{8.22}
\]

From these two equations it follows that
\[
G' = (1 + P) \frac{1}{2} G, \quad \text{and} \quad \tag{8.23}
\]
\[
G' = (1 - P) \frac{1}{2} G. \tag{8.24}
\]

Using these expressions we can write equation (8.22) as
\[
G = (1 + P) \frac{1}{2} G + (1 - P) \frac{1}{2} G. \tag{8.25}
\]

The desired expression for $G$ is obtained by replacing both the $\frac{1}{2}G$’s with use of the zero polarization forms of equations (8.23) and (8.24):
\[
G'_{p=0} = \frac{1}{2} G, \quad \text{and} \quad \tag{8.26}
\]
\[
G'_{p=0} = \frac{1}{2} G. \tag{8.27}
\]
This results in
\[ G = (1 + P) G_{P=0}^\uparrow + (1 - P) G_{P=0}^\downarrow. \] (8.28)

This expression is equivalent to equation (8.19) and it tells us that the appropriate weight-
ing factors for the spin-up and spin-down conductance are \((1+P)\) and \((1-P)\), respectively, thus
\[ \frac{G_{\text{NS}}}{G_{\text{NN}}} = (1 + P) \left( \frac{G_{\text{NS}}}{G_{\text{NN}}} \right)^\uparrow + (1 - P) \left( \frac{G_{\text{NS}}}{G_{\text{NN}}} \right)^\downarrow. \] (8.29)

Usually, the conductance curves calculated with equation (8.29) are in good agreement with experiment. To extract most accurate values of the tunneling polarization, however, it is necessary to include two corrections on the spin-split superconducting density of states. These corrections are considered next.

### 8.3 Corrections on the BCS density of states

The electron system of a superconductor can be divided into three systems. There is the condensate of Cooper pairs, the system of unpaired spin-up electrons, and the system of unpaired spin-down electrons. Often the unpaired electrons are referred to as quasi-
particles, however, for simplicity here they will be referred to as electrons. So far the three systems are considered as independent, i.e. any interaction between them is neglected. By taking two interactions into account, however, a better agreement with experiment and, accordingly, a more accurate extraction of the tunneling polarization is obtained. The interactions are illustrated by the diagram shown in figure 8.1.

The interaction between the condensate and the unpaired electrons is referred to as depairing. Its strength is measured by the dimensionless depairing parameter \(\zeta\). Due to this interaction electrons continuously enter and leave the condensate, i.e. the Cooper pairs and the unpaired electrons have a limited lifetime.

The second interaction is the spin-orbit interaction, which is responsible for the transfer of electrons between the spin-up and spin-down system. The effect of this interaction is measured by the dimensionless spin-orbit scattering parameter \(b\). Before the origin of the interactions and their influence on the spin-split superconducting density of states are discussed, we first consider how \(\zeta\) and \(b\) are incorporated into the theory.

For the independent spin-up and spin-down electron systems, the normalized electron energies \(u\) and \(d\) are given by equations (8.17) and (8.18), respectively. In general, the energy spectrum of a system changes when an interaction with another system is introduced. Likewise, in a superconductor the depairing and the spin-orbit interaction have an effect \(u\) and \(d\). In presence of the interactions, \(u\) and \(d\) are given by [73]

\[
\begin{align*}
  u &= \frac{E - \mu_B B}{\Delta} + \zeta \frac{u}{\sqrt{1 - u^2}} + b \frac{d - u}{\sqrt{1 - d^2}} \\
  d &= \frac{E + \mu_B B}{\Delta} + \zeta \frac{d}{\sqrt{1 - d^2}} + b \frac{u - d}{\sqrt{1 - u^2}}.
\end{align*}
\] (8.30) (8.31)
Figure 8.1: Illustration of the interactions between the spin-up electrons, spin-down electrons, and the condensate of Cooper pairs.

The $\zeta$-term and $b$-term can be regarded as corrections on the independent electron energies. Because $u$ and $d$ no longer depend explicitly on $E$, they need to be solved self-consistently using numerical procedures [74]. The conductance curves considered in this thesis are thus calculated with equation (8.29) by using the self-consistently solved $u$ and $d$ in equations (8.15) and (8.16), respectively.

**Depairing**

Generally, depairing in a superconductor is caused by the presence of a magnetic field. The field can originate from different sources. It can be due to magnetic impurities, it can be the current-generated field when the superconductor carries a current, or, most relevant for our purpose, the field may simply be an external applied field [75]. The action of the field is to induce an orbital motion of the electrons by the Lorentz force. This breaks up the pairs since the orbital motion is incompatible with the symmetry requirements for two paired electrons.

Here we consider the depairing in the aluminum superconducting electrode induced by an external field applied roughly in the plane of the superconductor. The field has an in-plane component $B_\parallel$ and a relatively small component $B_\perp$ perpendicular to the plane. The thickness $t$ of the superconductor is small as compared to the penetration depth of the in-plane field. Accordingly, the field penetrates the superconductor uniformly, and the depairing parameter $\zeta$ is a constant in the superconductor. The depairing parameter can be expressed as [75, 76]

$$\zeta = \zeta_0 + \frac{\tau_m v_F (ev_F B_\perp)}{3\Delta} + \frac{\tau_m t^2 (ev_F B_\parallel)^2}{18\hbar \Delta}, \quad (8.32)$$
where $\tau_m$ is the momentum scattering time and $v_F$ the Fermi velocity. The second term is the depairing induced by the perpendicular field and the third term the depairing induced by the in-plane field. The parameter $\zeta_0$ is the depairing induced by sources other than the applied field. Note that $e v_F B_\perp$ and $e v_F B_\parallel$ are the Lorentz forces acting on the electrons. With $B_\perp = B_\parallel = B$, the ratio between the perpendicular and the in-plane term is $6\hbar/\ell^2 eB$. 

**Figure 8.2:** Conductance calculated with different values of the depairing parameter $\zeta$ in zero field (a) and with a Zeeman splitting of $0.6\Delta$ (b). In the zero field case (a), the trend in the conductance with increasing $\zeta$ is indicated by the arrows.
With a typical thickness of several nm and a field of a few Tesla, this number is $10^4$. Apparently, a perpendicular field is a much more effective pair breaker than an in-plane field. This is because the orbital motion induced by the in-plane field is perpendicular to the superconductor, and therefore effectively quenched by the limited film thickness. On the other hand, the orbital motion induced by the perpendicular field is in-plane with the superconductor and therefore only disturbed by the momentum scattering.

The effect of $\zeta$ on the conductance in absence of Zeeman splitting is shown by the curves in figure 8.2-(a). The arrows indicate the trend in the conductance with increasing $\zeta$. The depairing reduces the width of the energy gap and leads to a rounding of the maxima at the energy gap edge. In experiment, curves like these can be encountered, for example, when there is a small but effective perpendicular magnetic field present (see section 9.3), or when the superconductor contains a significant amount of magnetic impurities. Also, the trend in the curves is similar to what is observed when the temperature is increased.

Figure 8.2-(b) shows the effect of depairing in presence of Zeeman splitting. Due to the rounding of the conductance maxima the Zeeman splitting is less resolved in the curve calculated with $\zeta = 0.16$. Such a curve can be encountered, for example, when the superconductor is misaligned with the field (see section 9.3). Let us estimate the angle of misalignment corresponding to $\zeta = 0.16$, by ignoring the first and last term in equation (8.32) and calculating the magnitude of $B_\perp$. To this end we assume that the mean free path $\ell$ of the electrons in the aluminum is about 10 nm, which is comparable to the aluminum thickness. With a Fermi velocity $v_F$ of $10^6$ m/s, the momentum scattering time $\tau_m = \ell/v_F$ then becomes $10^{-14}$ s. Using these numbers and a $\Delta$ of 0.3 meV, the perpendicular field $B_\perp$ is several mT. The Zeeman splitting in figure 8.2-(b) of $0.6\Delta$ is induced by an in-plane field of 3 T. From this field and the perpendicular field it follows that the angle of misalignment is roughly $0.05^\circ$.

We have thus estimated that in a typical spin-polarized tunneling experiment the depairing due to a misalignment as small as $0.05^\circ$ leads to a significantly rounded conductance curve such as shown in figure 8.2-(b). This is in agreement with the observations discussed in section 9.3.

**Spin-orbit interaction**

This chapter ends with a consideration of the spin-orbit interaction and its influence on the Zeeman-split superconducting density of states.

An electron travelling through a metal is continuously passing positively charged nuclei. From the electrons perspective the nuclei are moving and thus constitute an electric current. This current generates a magnetic field experienced by the travelling electron. The spin-orbit interaction is the interaction between this magnetic field and the electron magnetic moment. When the electron is scattered, there is a probability that the scattering event is accompanied by a spin-flip. Since the spin-orbit interaction directly involves the electron magnetic moment, i.e. the electron spin, it is a driving force for the spin-flip process. This driving force is roughly proportional to the fourth power of the nuclei charge, i.e. the atomic
Figure 8.3: Conductance of a N/S tunnel junction calculated with different values of the normalized spin-orbit scattering rate $b$. The rates 0.02, 0.07, 0.70 and 7.00 correspond to the superconductors Al, V, Nb and Ta, respectively.
number $Z$ \cite{56, 57}. Accordingly, the spin-flip scattering rate $1/\tau_{so}$ can be expressed as

$$\frac{1}{\tau_{so}} \propto Z^4 \frac{1}{\tau_m}.$$  

(8.33)

The spin-flip scattering rate is usually referred to as the spin-orbit scattering rate. The parameter $b$ introduced above is the dimensionless spin-orbit scattering rate defined by

$$b = \frac{\hbar}{3\Delta} \frac{1}{\tau_{so}}.$$  

(8.34)

From the $b$-term in equations (8.30) and (8.31), it can be seen that the spin-orbit interaction has an effect only when the normalized electron energies $u$ and $d$ are split by the Zeeman energy $\mu_B B$. That is, the effect of spin-orbit scattering on the conductance is only visible in presence of a field. The effect of $b$ on the Zeeman-split superconducting density of states is visible from the calculated conductance curves in figure 8.3. Again the curves are calculated with a temperature and field typically encountered in experiment. The value of $b$ is increasing from bottom to top. The curves show that the spin-orbit scattering tends to merge the two spin-split densities of states together. When $b$ is sufficiently large the spin-up and spin-down density of states are merged completely and, despite the presence of the Zeeman energy, the measurement appears as if no field is applied.

From the tunnel junctions with aluminum electrodes described later in this thesis, typically a value for $b$ of 0.02 is found, which is consistent with earlier work \cite{58, 62}. Since $\Delta$ is about 0.3 meV, this corresponds to a spin-flip or spin-orbit scattering time with an order of magnitude of $10^{-11}$ s. From junctions with a superconducting vanadium electrode, a value of $b$ of 0.07 is determined \cite{58}, which is larger as compared to aluminum due to the larger atomic number. At first glance the curves with $b = 0.02$ and 0.07 hardly differ from the $b = 0.00$ curve. However, when the spin-orbit scattering is neglected and the tunneling spin polarization is determined simply from the relative differences in the peak heights as described in the previous chapter, one finds that typically the polarization found is a few % smaller than the correct value \cite{58}. Thus, it is useful to take the spin-orbit interaction into account.

The calculated curves in figure 8.3 demonstrate that the Zeeman-split density of states is clearly observable with use of aluminum and, in principle, also with vanadium. For the heavier superconductors niobium and tantalum, which are located below vanadium in the periodic table of the elements, one can estimate $b$ by extrapolation of the vanadium value to the appropriate atomic number with use of equation (8.33). For niobium then one finds $b = 0.70$ and for tantalum $b = 7.00$. The curves calculated with these normalized spin-orbit scattering rates show that it is in principle extremely difficult to perform spin-polarized tunneling with these superconductors.
Chapter 9

Experimental

This chapter describes the preparation of the tunnel junctions, the cryogenic system used to cool them below 0.3 K, and introduces X-ray photoelectron spectroscopy. This surface analysis technique is used for structural characterization of the junctions. For a description of the electronics used for the conductance measurement, the reader is referred to section 4.3.

9.1 Junction preparation

The tunnel junctions used in this thesis are prepared by sputter-deposition and plasma oxidation. Crucial for spin-polarized tunneling experiments is the ability to prepare a superconducting electrode which has a sufficiently high critical field and transition temperature. These and other aspects of the superconducting electrode are described separately in the next chapter. This section describes the basics of the sputter-deposition and plasma oxidation technique, and the junction preparation procedure.

Sputter-deposition

The principle of the sputter-deposition technique [77] is shown in figure 9.1. The substrate is positioned below the target of the material which is to be deposited. The sputter target is at negative potential with respect to a ring-shaped anode. The voltage difference creates an argon plasma below the target. The positively charged argon ions are accelerated towards the target and knock the target atoms loose, ejecting them into the volume below the target. This process is known as sputtering. The use of a noble gas such as argon ensures that the target atoms do not react with the ions to any significant degree, such that the target atoms diffuse outwards and coat the substrate. The argon plasma, and consequently the deposition rate, is stable within a limited pressure and voltage window. The argon gas injected in the deposition chamber prior to sputtering is of limited purity. In industrially purified argon the impurities consist mainly of oxygen and water molecules. During deposition, the impurities are incorporated in the deposited layer. To minimize
the contamination of the deposited layer, sputtering is performed with the lowest possible argon pressure. The minimum pressure at which the plasma is stable is reduced significantly by placing a permanent magnet above the sputter target. The magnetic field penetrates through the target into the plasma and forces the charged particles in the plasma to move in helical orbits, essentially confining them in a smaller volume [77]. Sputtering with use of such a magnetic field is referred to as magnetron sputtering.

The sputter-deposition is performed in a vacuum chamber with a base pressure in the low $10^{-8}$ mbar range achieved without baking. The chamber is equipped with six magnetron sputter sources and a dedicated sample stage [78]. The sputter sources are designed for 2 inch diameter targets and the sample stage allows for positioning of the substrate under individual sources. The deposition rate is roughly proportional to the power supplied by the voltage source, i.e. the deposition rate increases with the applied voltage. Deposition on the substrate is started and ended by opening and closing a shutter located in between the target and substrate. Preparation of tunnel junctions requires deposition with a thickness controllability on the angstrom scale. The thickness controllability is determined by the deposition rate and the time required for handling the shutter. Opening or closing the shutter takes about a quarter of a second. Therefore, only deposition times larger than one second can be timed accurately. When the voltage is close to the minimum at which the plasma is stable, the deposition rate from a typical metallic target is about 1 Å/s. This rate is sufficiently low to obtain the desired thickness accuracy.

The argon pressure during deposition is roughly $10^{-2}$ mbar. The argon gas has a 99.999 % purity (grade 5), meaning that the partial impurity pressure is roughly $10^{-7}$ mbar. With elementary vacuum theory it can be estimated that in an atmosphere of $10^{-7}$ mbar

![Figure 9.1: Principle of sputter-deposition.](image-url)
and with a sticking factor of 0.1, a clean surface is covered in roughly 100 seconds. With an atom diameter of 1 Å, this corresponds to a contamination rate of roughly 0.01 Å/s, two orders of magnitude lower than the deposition rate. Consequently, the deposited layers contain percent amounts of impurities. This amount can be reduced straightforwardly by using argon gas of higher purity and by increasing the deposition rate. In most cases, however, such measures do not result in observable changes in the junction parameters, such as the tunneling spin polarization, indicating that in general the impurity level is too low to be of any significant influence. One exceptional case where the impurity level is of significant influence is described in section 10.3.

Plasma oxidation

The technique used for preparation of the tunnel barrier is plasma oxidation of a metallic film, i.e. an exposure to the afterglow of an oxygen plasma [78, 79]. Plasma oxidation is performed in a separate vacuum chamber connected to the deposition chamber, to which the sample can be transported while it is kept under vacuum conditions. The vacuum chamber, referred to as the oxidation chamber, has a base pressure lower than $10^{-8}$ mbar. The sample is positioned below two ring-shaped electrodes as shown schematically in figure 9.2. The oxidation is started by applying a voltage over the electrodes and subsequently injecting an amount of oxygen gas into the chamber. The electric field between the electrodes instantaneously ionizes the oxygen gas, resulting in an oxygen plasma. Electron-oxygen collisions generate various ions, excited atoms and molecules [79]. In figure 9.2 the excited oxygen particles are denoted with $O^*$. The ions and electrons are accelerated towards the negative and positive electrode, respectively, while the neutral $O^*$ particles reach the sample where they react with the metallic film.

For the work described in this thesis, junctions with AlO$_x$, MgO, and TaO$_x$ barriers are prepared. The sputter-deposited aluminum, magnesium and tantalum metal films are oxidized with a fixed oxygen pressure of $10^{-1}$ mbar and a plasma power of 5 W. Independent optical monitoring of the oxidation process [79] shows that the oxidation of...
these films is self-limited and occurs essentially in the first 200 s. The oxygen plasma exposure is stopped after 200 s, accordingly. The thickness of the metal film fully oxidized by the 200 s plasma exposure can be determined from optical transmission measurements on films of different thicknesses deposited on glass [78]. This measurement exploits the large optical contrast between the metal and its oxide. The metal has a high reflectivity and the oxide is transparent. The thickness of the metal film fully oxidized after 200 s is about 20, 25 and 15 Å for Al, Mg and Ta, respectively. These thicknesses are used as the first guess for the thickness of the barrier film.

In addition to the excited oxygen atoms, also oxygen molecules present in the oxidation chamber outside the plasma react with the film, i.e. the film also oxidizes without the plasma. This type of oxidation is referred to as thermal oxidation. For the preparation of tunnel barriers in general, plasma oxidation is preferred over thermal oxidation since it is faster and, particularly in the case of AlO$_x$ barriers, plasma oxidation has proven to result in higher TMR effects [79].

**Preparation procedure**

The junctions are deposited on glass substrates, in particular 1 mm thick barium borosilicate glass sheets provided by Corning Inc. (glass code 7059). The substrates are cleaned *ex-situ* by an ultrasonic ammonia bath for several minutes and, subsequently, rinsed with isopropanol. After this cleaning procedure the substrate is fixed on a substrate holder and loaded into the sputter-deposition chamber via a load-lock. Before deposition, the substrate surface is cleaned *in-situ* by exposing it to an oxygen plasma in the oxidation chamber for ten minutes. This procedure converts any hydrocarbon residues left from the *ex-situ* cleaning procedure into volatile carbon oxides and water vapor which are pumped away leaving a significantly cleaner surface.

As will be explained in the next chapter, the aluminum electrode should be made as thin as possible. During the development stage of the junction preparation procedure, it has been found that with glass substrates significantly thinner closed metallic aluminum films can be prepared as compared with silicon wafers. This difference is probably due to a smaller surface roughness of the glass substrates. The surface of the glass is formed at high temperature when the glass is slowly cooled from the liquid phase to the glass phase, while the surface of the Si wafer consists of SiO$_x$, formed at room temperature during the first exposure of the wafer to air. The large difference in the temperature at which the SiO$_x$ surface has formed is most likely responsible for the smaller roughness of the glass sheets.

The lateral dimensions of the junction area and the electrodes are defined using a metal shadow mask during deposition. Before the deposition of the bottom electrode, the shadow mask is placed on top of the substrate as shown in figure 9.1 by means of a magnetically coupled manipulator. After the deposition the mask is removed. At this stage the sample looks as shown in figure 9.3-(a). The electrode is a strip with a length of roughly 1 cm and a width of 400 µm. At both ends the strip is wider to facilitate electrical connections.
The cross-section of the strip shows that the edges are wedge-shaped over a distance of roughly 50 µm independent of the deposited thickness [78]. This is caused by screening of the deposition at the edges by the finite thickness of the mask. The next step is the deposition of the metal film to be oxidized by the oxygen plasma exposure. In general, this film is deposited without mask, i.e. the film is deposited on the entire substrate area. In this way an inhomogeneous thickness of the barrier on the final junction area due to screening by the mask edges is avoided. Subsequently, the sample is exposed to the oxygen plasma in the oxidation chamber, transforming the barrier film into oxide. Due to the transparency of the glass substrate, the optical contrast between the light-gray colored metal film and the transparent oxide is clearly visible by eye. This contrast is illustrated by figure 9.3-(b) and (c). The glass substrate thus provides extra convenient monitoring during junction preparation. For the deposition of the top electrode, the mask is rotated by 90 degrees and placed back on the substrate. The finished junction is shown in figure 9.3-(d). For simplicity one junction is shown, while, actually, the mask is designed such that in a single deposition 14 strips are deposited which, after the 90 degree rotation, result in 4 sets of 6 independently measurable junctions.

The lateral dimensions of the junction area are 400 by 400 µm, determined by the width of the strip in the shadow mask. For the development of tunnel junction devices compatible with semiconductor technology, much smaller junctions with dimensions on the scale of 1 µm are prepared by others using post-deposition patterning. Here the deposition is performed without a shadow mask and isolated junctions are obtained with optical lithography and etching procedures. For the purpose of the work described in this thesis, small junction dimensions are not crucial and therefore the relatively easy and fast preparation with a shadow mask is most suitable.

![Figure 9.3: Cross-section and top view of the junction after deposition of the bottom electrode (a), deposition of the barrier film (b), oxygen plasma exposure (c), and deposition of the top electrode (d).]
More on preparation

In figure 9.3 the thickness of the bottom electrode is drawn to be much thinner as compared to the top electrode. This is representative for the case of an Al/barrier/N junction, described in more detail in the next chapter, in which the Al electrode is the relatively thin bottom electrode and N the ferromagnetic electrode deposited on top of the barrier. The total thickness of the aluminum electrode and the barrier is smaller than 50 Å, while the ferromagnetic top electrode has a thickness of 200 Å. Usually, the ferromagnetic top electrode is capped with a tantalum layer of 60 Å. The self-limiting oxide of tantalum protects the ferromagnet from oxidation. In case of an N/barrier/Al junction, of which the superconducting aluminum electrode is deposited on top of the barrier, tantalum, or most other metals, cannot be used as a capping layer because they will quench the superconducting transition temperature. Instead of depositing a capping layer, an extra in-situ oxygen plasma exposure is applied creating a clean protective AlO$_x$ layer. To minimize the interface roughness of N/barrier/Al junctions, the ferromagnetic bottom electrode is not deposited directly on the substrate but on a tantalum buffer layer [78].

Important for the choice of materials for the junction preparation and the interpretation of experimental results, is the consideration of the chemical stability of the barrier oxide at the interfaces with the electrodes (see chapters 11 and 12). By comparing the energies of formation of the barrier oxide and the electrode oxide, it can be deduced whether it is to be expected that a particular interface is chemically stable [78, 80]. Some relevant interfaces are considered in table 9.1.

As an example here we consider the Al$_2$O$_3$/Co interface, particularly relevant for magnetic tunnel junctions. From the comparison between the formation energies of Al$_2$O$_3$ and Co$_3$O$_4$, which is the most stable stoichiometry of the Co oxides, it follows that it is energetically favorable for the oxygen atoms to be bond to Al rather than Co. X-ray

<table>
<thead>
<tr>
<th>interface</th>
<th>reaction</th>
<th>stable?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$/Co</td>
<td>4Al$_2$O$_3$ + 9Co ← 8Al + 3Co$_3$O$_4$</td>
<td>yes</td>
</tr>
<tr>
<td>Al$_2$O$_3$/Gd</td>
<td>Al$_2$O$_3$ + 2Gd → Gd$_2$O$_3$ + 2Al</td>
<td>no</td>
</tr>
<tr>
<td>MgO/Gd</td>
<td>3MgO + 2Gd ↔ Gd$_2$O$_3$ + 3Mg</td>
<td>?</td>
</tr>
<tr>
<td>Al/MgO</td>
<td>3MgO + 2Al ← Al$_2$O$_3$ + 3Mg</td>
<td>yes</td>
</tr>
<tr>
<td>Al/Ta$_2$O$_5$</td>
<td>3Ta$_2$O$_5$ + 10Al → 5Al$_2$O$_3$ + 6Ta</td>
<td>no</td>
</tr>
<tr>
<td>Al/HfO$_2$</td>
<td>3HfO$_2$ + 4Al ← 2Al$_2$O$_3$ + 3Hf</td>
<td>yes</td>
</tr>
<tr>
<td>Ta$_2$O$_5$/V</td>
<td>Ta$_2$O$_5$ + 2V ← V$_2$O$_5$ + 2Ta</td>
<td>yes</td>
</tr>
<tr>
<td>Al$_2$O$_3$/V</td>
<td>5Al$_2$O$_3$ + 6V ← 3V$_2$O$_5$ + 10Al</td>
<td>yes</td>
</tr>
<tr>
<td>Al$_2$O$_3$/Mn</td>
<td>4Al$_2$O$_3$ + 9Mn ← 3Mn$_3$O$_4$ + 8Al</td>
<td>yes</td>
</tr>
<tr>
<td>Co$_3$O$_4$/Mn</td>
<td>Co$_3$O$_4$ + 3Mn → Mn$_3$O$_4$ + 3Co</td>
<td>no</td>
</tr>
</tbody>
</table>

Table 9.1: Chemical stability of relevant interfaces. Adapted from [78, 80].
photoelectron spectroscopy measurements, explained later in section 9.4 and considered in chapters 11 and 12, confirm that the interface is indeed chemically stable. In other words, when cobalt is deposited or the junction is heated to elevated temperatures, it is not able to steal oxygen from the Al₂O₃ barrier. In the next chapters we will further refer to table 9.1.

9.2 Sorption-pumped ³He refrigerator

As explained earlier in section 7.3, the junctions need to be cooled below 1 K to make the thermal broadening of the Fermi level sufficiently small to allow for clear observation of Zeeman splitting in an applied field of several Tesla. With a cryogenic system based exclusively on common liquid helium, typically a boiling temperature around 1.2 K can be reached by reducing the vapor pressure above the liquid. Such a system does not meet our requirement. The junctions are cooled by a system which makes use of an amount of the rare ³He isotope instead of common ⁴He. This system is referred to as the sorption-pumped ³He refrigerator. By reducing the vapor pressure above liquid ³He, the refrigerator is capable of cooling the junctions below 0.3 K, making use of the higher volatility of ³He [81].

The sorption-pumped ³He refrigerator is part of a Heliox VL (vacuum loading) system provided by Oxford Cryogenics, shown schematically in figure 9.4. The system consists of a common ⁴He bath cryostat and an insert. The bottom part of the insert consists of a vacuum chamber, which contains the sorption-pumped ³He refrigerator and two samples with six junctions each. The samples are thermally connected to the coldest part of the ³He refrigerator via a rotator mechanism and gold-plated copper rods. The coldest part of the refrigerator is the so-called ³He pot and the rods are referred to as cold fingers. The rotator mechanism allows for alignment of the samples parallel to the vertical magnetic field, which is generated by the superconducting coil located in the ⁴He bath. The coil is capable of generating a maximum field of 8 Tesla.

We will briefly discuss how the samples are taken out of the system, how they are loaded into the system, and how they are cooled to 4.2 K. After that, we will discuss the operation of the sorption-pumped ³He refrigerator, which cools the samples further to a temperature below 0.3 K.

The samples are taken out by, subsequently, lifting the entire insert out of the cryostat, leaving it to warm up to room temperature, venting the vacuum chamber via the pump connection at the top of the insert, and by removing the cylinder-shaped vacuum case. When the vacuum case is removed the samples can be exchanged. The loading procedure starts by, subsequently, placing the vacuum case back, pumping the vacuum chamber down to a rough vacuum, and injecting a small amount of helium gas into the vacuum chamber. After this, the insert is slowly lowered into the cryostat while the cryostat is sealed with a sliding seal. During this period of roughly 45 minutes, the ³He refrigerator and the samples are cooled from room temperature to 4.2 K due to the thermal conductivity of the helium gas in the vacuum chamber. Since the insert is lowered slowly, mainly the enthalpy of the cold helium gas present above the bath is used for cooling, and, accordingly, a minimum
Figure 9.4: Overview of the Heliox VL system.
amount of liquid helium is consumed.

Once the insert is lowered completely, as drawn in figure 9.4, the samples are cooled further by the $^3$He refrigerator. During operation of the $^3$He refrigerator, however, the thermal conductivity of the helium gas in the vacuum chamber is undesired. The gas is pumped out of the vacuum chamber by a piece of charcoal. When charcoal is cooled below 20 K, helium gas starts to adsorb on its very large surface area. The adsorption speed increases exponentially as the temperature is lowered. When the insert is lowered completely, the charcoal is at 4.2 K and the $^3$He refrigerator is thermally isolated from the $^4$He bath.

The sorption-pumped $^3$He refrigerator is shown in more detail in figure 9.5-(a). The $^3$He is contained in a closed hourglass-shaped chamber. The upper volume of the chamber contains a charcoal sorption pump equipped with a heater. The lower volume of the chamber is the $^3$He pot which is in thermal contact with the samples. The upper and the lower volume are connected via a neck. The neck can be cooled with $^4$He, which is taken from the $^4$He bath with a pick-up tube and passed through a needle valve. The tube is wrapped around the neck a few times, passes through the charcoal sorption pump and finally terminates at the top of the insert where it is connected to a pump.

The $^3$He pot is cooled to a temperature below 0.3 K by first condensing an amount of $^3$He and then reducing the vapor pressure above the liquid with the sorption pump.

![Figure 9.5: The sorption-pumped $^3$He refrigerator and its operation.](image-url)
Figure 9.5-(b) shows the refrigerator during the condensation of $^3$He. During condensation, the sorption pump is kept above 20 K with the heater. At this temperature, $^3$He desorbs from the charcoal surface. When $^4$He is pumped through the needle valve, expansion causes its temperature to drop to a value below 4.2 K depending on the position of the needle valve. The $^4$He flow cools the neck below the boiling temperature of the $^3$He gas which causes it to condense on the wall of the neck. The condensed $^3$He drips down into the $^3$He pot where the liquid accumulates. Initially the $^3$He condenses at 2.7 K. For the condensation to proceed, it is necessary to cool the neck gradually to lower temperature since the $^3$He pressure and, accordingly, the boiling temperature decrease. Usually after about 20 minutes, the temperature has reached 1.5 K and roughly 2 cm$^3$ liquid $^3$He has accumulated in the $^3$He pot. At this temperature the condensation is stopped by switching the heater of the sorption pump off. In addition to the neck, also the sorption pump is cooled by the $^4$He flow. After the heater has been switched off, the sorption pump cools to a temperature below 20 K and it starts to lower the $^3$He vapor pressure. Within several minutes, the $^3$He pot can be pumped down to below 0.4 K. After half an hour the sorption pump is cooled below 3 K and the $^3$He pot has reached a base temperature of 0.25 K. Figure 9.5-(c) shows the refrigerator when it is running at base temperature. The base temperature can be maintained as long as liquid $^3$He is present. Under normal conditions it takes several days for all the liquid to evaporate, much longer than the time required for the measurements.

### 9.3 Magnetization and alignment

Once the junctions are cooled to base temperature, conductance-voltage characteristics are measured. The measurement method and electronics used are equivalent to what is described in section 4.3. For proper characterization of the junctions, two procedures are of crucial importance, namely, magnetization of the ferromagnetic electrode and the alignment of the junction with the magnetic field. We will first discuss the magnetization and after that the alignment.

When the magnetization of the ferromagnet is not homogeneous over the entire electrode but divided over multiple domains, a domain wall may be present within the junction area. At this domain wall the magnetic field generated by the magnetization can have a significant component perpendicular to the plane of the junction. This magnetic field penetrates through the barrier into the superconductor. As discussed earlier in section 8.3, a perpendicular magnetic field is an effective source of depairing and, therefore, has a negative influence on the superconducting density of states. To demonstrate the importance of this influence, we consider the example shown in figure 9.6-(a). The zero-field gap of an Al/AlO$_x$/Co junction is measured before and after the cobalt electrode is magnetized by application of an in-plane field. Before application of the field (black markers), the superconducting gap is affected by the perpendicular magnetic field originating from the domain walls in the cobalt electrode. After application of the field (open markers), the superconducting gap has significantly sharper maxima at the energy gap edge. The effect
Figure 9.6: Measurements of an Al/AlO$_x$/Co junction at 0.3 K showing the zero-field gap before and after application of an in-plane field of 3 T for 15 minutes (a), and the effect of a misalignment of roughly 0.2° in an applied field of 3.5 T (b).

The example demonstrates that magnetization of the ferromagnetic electrode before measurements are performed is necessary. It has been found that the magnetization of a cobalt electrode at 0.3 K requires a field strength of several Tesla during at least ten minutes.
When the magnetic field is applied to Zeeman-split the superconducting density of states, it is necessary to minimize depairing by aligning the superconducting electrode with the field. For alignment of the samples the insert is equipped with a rotator mechanism which can be operated manually by turning a knob at the top of the insert (see figure 9.4). The mechanism allows for rotation of the samples on a scale of 0.025°. Usually, before the alignment procedure the rotator is still in the position used for the measurement of earlier samples, and, therefore, the samples are already within 0.5° from the optimum angle. Before alignment the measurement may look as the black curve shown in figure 9.6-(b). In this particular example a Al/AlO\textsubscript{x}/Co junction is measured in a field of 3.5 T. When the angle between the sample and the field is reduced, the decreased depairing leads to an increase of the conductance maxima and a decrease in the conductance minima. The alignment is done by minimizing the zero bias conductance through rotation of the sample in steps of 0.025°. In the case shown in figure 9.6-(b), the alignment procedure has changed the angle with 0.2°. The conductance measured after the alignment (open markers) shows larger maxima and deeper minima. The significant influence of a misalignment as small as discussed here, was predicted earlier in section 8.3 (see figure 8.2-(b)).

9.4 X-ray photoelectron spectroscopy

Complementary to the conductance measurements, the junctions have been characterized with in-situ X-ray photoelectron spectroscopy (XPS). More specific, as described in chapters 11 and 12, XPS has been used to investigate AlO\textsubscript{x} and MgO tunnel barriers, various barrier/ferromagnet interfaces and diffusion of foreign atoms. In this section XPS is introduced. A more complete overview of XPS and its capabilities can be found elsewhere [82].

XPS is a measurement technique for quantitative and qualitative chemical analysis of the atoms present in the topmost 10 to 20 Å below the surface of a sample. The principle of XPS is illustrated in figure 9.7. The sample under investigation is exposed to monochromatic X-ray radiation of a known fixed energy. The energy of the X-ray photons is high enough to excite electrons from the atomic energy levels to an energy above the Fermi level. In figure 9.7 this process is shown with an electron from a 2\textit{s} level. Part of the excited electrons, referred to as photoelectrons, escape from the sample in the direction of a spectrometer which measures the number of photoelectrons as a function of kinetic energy. As energy is conserved, the kinetic energy of the photoelectrons is equal to the difference between the photon energy and the binding energy of the atomic level. Consequently, the kinetic energy spectrum measured by the spectrometer essentially resembles the spectrum of the atomic levels.

The X-rays penetrate a substantial distance of several µm into the sample. The surface sensitivity of XPS originates from the fact that only the photoelectrons generated in the topmost 10 to 20 Å below the surface are able to escape from the sample. Photoelectrons generated deeper in the sample lose all their kinetic energy before they arrive at the surface through inelastic scattering. Also the photoelectrons that arrive at the spectrometer but are generated several angstroms below the surface, have a probability to scatter and lose a
part of their kinetic energy before they escape. These electrons have an arbitrary kinetic energy and therefore give rise to a background intensity in the kinetic energy spectrum. Usually, the sample is positioned with the surface perpendicular to the aperture of the spectrometer as shown in figure 9.7. In this situation the photoelectrons emitted in a direction perpendicular to the surface are detected. The surface sensitivity can be enhanced, i.e. the intensity from photoelectrons generated below the surface can be suppressed, by rotating the sample such that only photoelectrons emitted in a direction under grazing angle with the surface are detected. In this way the effective escape depth can be reduced with a factor 3.

To introduce more aspects of XPS we consider, as an example, the series of spectra shown in figure 9.8. The spectra are taken from a single sample at different stages. As is common for XPS, the kinetic energy spectrum is shifted in energy by a subtraction of the X-ray photon energy. In this way the spectrum is more conveniently plotted as a function of the binding energy. The spectrum taken first (bottom) is that of a clean 40 Å aluminum film deposited on glass. The electronic configuration of aluminum is $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p$. The binding energy of the deep $1s$ level is 1558 eV. The X-ray photon energy used, however, is 1487 eV, not high enough to eject $1s$ electrons. The $3s$ and $3p$ electrons constitute the valence band of which the bottom is located roughly at 10 eV. The part of the spectrum shown includes the $2p$ level at 73 eV and the $2s$ level at 118 eV. The background intensity is caused by inelastic scattering of the photoelectrons ejected from the valence band. The
The $2p$ level of the silicon in the glass substrate is located at 99 eV. At this energy, however, no peak is visible as the photoelectrons generated in the glass are not able to escape from the sample.

In addition to the $2p$ and $2s$ levels, some secondary structure on the right and the left of the main levels is visible. The X-ray radiation is not completely monochromatic but contains a second small intensity of photons with 10 eV higher energy. These photons are

\[ \text{Figure 9.8: The examples of XPS spectra as discussed in the text.} \]
responsible for the small peak on the right of the main levels. Such a peak is referred to as a satellite. The peaks on the left of the main levels are due to photoelectrons who have lost part of their kinetic energy to excite a collective oscillation of the sea of conduction electrons. The energy quantum of such an oscillation is referred to as a plasmon. Since the conductance electrons at the surface behave differently from conduction electrons in the bulk of the film one can observe a surface plasmon and a bulk plasmon.

When chemical bonds between atoms are formed, the atomic levels are shifted in energy. Although these chemical shifts are relatively small, they can be resolved and therefore provide the extremely useful possibility to study the chemical environment of atoms. An example of a chemical shift is shown in the second spectrum of figure 9.8 (middle). This spectrum is taken after the topmost 15 to 20 Å of the aluminum film is oxidized by an exposure to an oxygen plasma. For clarity the spectrum is artificially lifted in intensity so that it does not overlap with the first spectrum. The bonds with the oxygen atoms have increased the binding energy of the aluminium levels with about 4 eV. Also note that, since there are no conduction electrons in AlO$_x$, the plasmon peaks have disappeared.

The last spectrum we consider is taken after the deposition of an amount of cobalt equivalent to a layer thickness of 4 Å. This spectrum, shown at the top in figure 9.8, demonstrates the possibility of studying the chemical state of atoms at an interface. The small amount of cobalt ensures that the large part of the cobalt atoms are in physical contact with AlO$_x$. Despite this extremely small amount, the 3s and 3p levels of the cobalt atoms are clearly observable and their binding energies can be determined unambiguously. In the work described in chapters 11 and 12, this particular approach is used to investigate different barrier/ferromagnet interfaces.
Chapter 10

The superconducting electrode

A spin-polarized tunneling experiment requires a tunnel junction which shows a good gap quality and has a superconducting electrode with a sufficiently high critical field. With good gap quality we mean that the conductance curve has the shape of the BCS density of states, implying that the conductance is zero at zero-bias and possesses sharp well-defined maxima at the edges of the superconducting energy gap. In this chapter we discuss examples of the gap quality and critical fields obtained with superconducting aluminum and vanadium electrodes in differently prepared tunnel junctions. These examples illustrate the difficulties encountered. First, however, we briefly recall the basic theory of the critical field of superconductors in general, and the critical field of aluminum films in particular.

10.1 The critical field

When a bulk superconductor is placed in a magnetic field, the field inside the superconductor is cancelled by a magnetic field generated by a screening current on the surface of the superconductor. The screening current and accordingly the surface energy of the superconductor increases with the external field strength. At the critical field, the magnitude of the surface energy makes it energetically favorable for the superconductor to make the transition to the normal state. Below the surface of the superconductor the field decays exponentially over a distance $\lambda$ measured from the surface. This distance is referred to as the penetration depth of the magnetic field. When in general the dimensions of the superconductor are comparable to $\lambda$, the field penetrates a significant part of the volume and the screening current is smaller as compared to a bulk superconductor. Accordingly, a smaller superconductor has a lower surface energy density and a higher critical field.

The critical field caused by the field-induced increase of the surface energy is described by the Ginzburg-Landau theory [75,83]. For a superconducting film with thickness $t$ and an electron mean free path small as compared to the superconducting coherence length $\xi$, a condition fulfilled by the films we are considering, the Ginzburg-Landau theory predicts
that the critical strength of a field applied parallel to the film is given by

\[ B_c \approx 6 B_c^{\text{bulk}} \left( \frac{\lambda \sqrt{\xi}}{t^{3/2}} \right), \quad (10.1) \]

where \( B_c^{\text{bulk}} \) is the critical field of the bulk superconductor. According to this equation the critical field increases without limit as the film thickness goes to zero. This can be understood as follows. When the film thickness is decreased, the field penetrates a larger part of the film and the screening current is smaller. Eventually, when the thickness is much smaller than \( \lambda \), the field penetrates the film uniformly and the screening current is zero. Thus, in the limit of zero film thickness there is no field-induced increase of the surface energy.

Equation (10.1) suggest that in experiment the highest critical field is obtained simply by making \( t \) as small as possible. However, in the Ginzburg-Landau theory it is assumed that the superconducting transition temperature \( T_c \) is independent of the film thickness, while in practice the \( T_c \) of essentially all superconductors decreases when the film becomes thinner. The \( T_c \) can be quenched below the experimentally achievable temperature even

![Diagram showing the thickness dependence of the critical field of aluminum films](image)

**Figure 10.1:** Thickness dependence of the critical field of aluminum films as measured by Tedrow and Meservey [83].
if no magnetic field is applied. In contrast to a suppression, aluminum films show an enhancement of the $T_c$ with decreasing film thickness. While the $T_c$ of bulk aluminum is 1.1 K, thin films can be superconducting above 2 K. Although not completely understood, this unique property is responsible for the successful use of aluminum as the superconductor in spin-polarized tunneling experiments.

Since aluminum films do not suffer from a $T_c$-suppression, they can be used to verify equation (10.1). Figure 10.1 shows the thickness dependence of the critical field as measured by Tedrow and Meservey [83]. For films thicker than 100 Å the thickness dependence is in agreement with equation (10.1) (dashed line). Below this thickness, however, the data deviates from equation (10.1) as the critical field increases only weakly with decreasing thickness. For a 30 Å film, for example, equation (10.1) predicts a critical field of roughly 20 T, while 5 T is observed.

Apparently there exists a limitation of the critical field not accounted for by the Ginzburg-Landau theory. This limitation originates from the field-induced energy decrease of the normal state, which is a consequence of the Pauli spin-paramagnetism of the electrons. The critical field limit can be calculated by equating the decrease of the normal state energy and comparing it to the binding energy of the Cooper pair condensate. Let us calculate the decrease in the normal state energy. When the field is applied, the energy of the spin-up electrons is lowered by $\mu_B B$ and the energy of the spin-down electrons is raised by $\mu_B B$ as shown in figure 10.2-(a). Initially, there is an equal number of spin-up and spin-down electrons and therefore the total energy has not changed. Quickly, however, spin-down electrons relax to spin-up states at lower energy via spin-flip processes. The

![Figure 10.2: Explanation of the decrease in the normal state energy induced by a magnetic field (a), and an energy diagram for explaining the limitation of the critical field from a microscopic point of view (b).]
resulting energy decrease is indicated by the hatched rectangle in the figure. The area of the rectangle is the number of spin-down electrons that flip their spin. The area is equal to the density of spin-down states $\frac{1}{2}\rho_n$ multiplied by $\mu_B B$. The energy shift of the rectangle, indicated by the arrow, is the average energy loss per spin-flip and is equal to $\mu_B B$. Accordingly, the total energy decrease is given by the area $\frac{1}{2}\rho_n \mu_B B$ multiplied by $\mu_B B$. The binding energy of the condensate, as calculated in the BCS theory [28], is given by $\frac{1}{4}\rho_n \Delta^2$. At the critical field, the energy decrease of the normal state and the binding energy of the condensate are equal,

$$\frac{1}{2}\rho_n \mu_B B_c^2 = \frac{1}{4}\rho_n \Delta^2,$$

from which it follows that

$$\mu_B B_c = \frac{1}{2}\sqrt{2} \Delta.$$  \hspace{1cm} (10.2)

In the Pauli spin-paramagnetic limit the critical field is thus proportional to the energy gap. The critical field can be expressed in $T_c$ by eliminating $\Delta$ from equation (10.3) with use of the BCS relation

$$2\Delta = 3.53 k_B T_c.$$  \hspace{1cm} (10.4)

With $k_B = 86 \mu eV/K$ and $\mu_B = 58 \mu eV/T$, this leads to

$$\frac{B_c}{T_c} = 1.86 \ T/K,$$

meaning that the critical field in Tesla is roughly twice the transition temperature in Kelvin.

The existence of the critical field limit can also be argued from a more simple microscopic point of view. To this end consider the energy diagram shown in figure 10.2-(b). The applied field Zeeman-splits the single-electron states in the superconductor. When the Zeeman splitting $2\mu_B B$ of the single-electron states is equal to $2\Delta$, empty spin-up electron states are available at the energy level of the Cooper pair condensate. Above this field strength, it is energetically favorable for the Cooper pairs to break up via a spin-flip process of the spin-down electron. Based on this picture one would guess that $\mu_B B_c$ is roughly given by $\Delta$, which is in agreement with equation (10.3).

To achieve a critical field that is as high as possible, the thickness of the aluminum electrodes in spin polarized tunneling are generally smaller than 50 Å. Accordingly, the aluminum superconductor is in the Pauli spin-paramagnetic limit, which means that the critical field is proportional to $T_c$. The relatively weak increase of the critical field with decreasing thickness below 100 Å, as shown in figure 10.1, is caused by the enhancement of the $T_c$. Therefore, a larger critical field is obtained when the enhancement of the $T_c$ is larger. We will discuss more on the $T_c$-enhancement of the aluminum electrode in the next section.
10.2 Aluminum electrodes

In this section we discuss the gap quality and the $T_c$ obtained with differently prepared junctions with aluminum electrodes. First we consider Al/AlO$_x$/N junctions, where the aluminum electrode is the bottom electrode. This configuration is mostly used in earlier work. After that, results obtained with N/barrier/Al junctions are presented. In these junctions the aluminum is deposited on top of the barrier.

Al/AlO$_x$/N junctions

Here we consider junctions with Al bottom electrodes deposited on glass substrates at room temperature. The AlO$_x$ tunnel barrier is formed by exposing the bottom electrode to an oxygen plasma (see section 9.1). Figure 10.3-(a) shows the room-temperature sheet conductance of the Al electrode measured on finished junctions as a function of the as-deposited aluminum thickness. The sheet conductance is zero below 30 Å, indicating that in total roughly 30 Å aluminum is oxidized. Part of this 30 Å is caused by oxidation at the surface of the substrate and surface roughness, and the other part is oxidized by the plasma-oxidation. Below 60 Å the sheet conductance increases with thickness in a linear fashion, while at larger thickness the increase is stronger. In other words, the conductivity of the electrode is not a constant but increases with thickness. The change in conductivity is due to an increase of the electron mean free path. At larger thickness the electron mean free path is larger since the average aluminum grain size is larger and scattering at the top and bottom boundaries of the electrode is of less influence.

Figure 10.3-(b) shows the zero-field energy gap measured at 0.3 K as a function of thickness. Included are some corresponding values for $T_c$ as calculated with equation (10.4). The critical field in this thickness range is limited by Pauli spin-paramagnetism and therefore proportional to the energy gap and $T_c$ as explained previously. The corresponding critical field scale is indicated by the right-hand axis in figure 10.3-(b).

As generally observed for aluminum, the energy gap and $T_c$ increase as the thickness goes to zero. An understanding of the microscopic origin of the $T_c$-enhancement is currently lacking. From earlier experimental work it has become clear that the enhancement is correlated with the average grain size [84, 85]. In a thinner film the average grain size is smaller and the $T_c$ is higher. The average grain size not only depends on the film thickness, but also on the deposition technique, deposition conditions, the substrate, and impurity atoms on the substrate. An example of the dependence on deposition conditions is shown in figure 10.3-(b). When the base pressure of the deposition chamber is in the $10^{-7}$ mbar range instead of $10^{-8}$ mbar (which is the case after only one day of pumping after the chamber has been opened), a significantly higher $T_c$ and critical field is obtained. Thus, counter-intuitively, aluminum electrodes with higher $T_c$’s and critical fields are obtained when the conditions in the deposition chamber are less clean. Probably, oxygen atoms present on the substrate prior to the deposition and oxygen atoms incorporated in the film during deposition make the average grain size smaller thereby enhancing the $T_c$. 

109
Figure 10.3: Thickness dependence of the aluminum electrodes in Al/AlOₓ/N junctions sputter-deposited on glass substrates at room temperature. The sheet conductance (a) indicates that in the finished junction a total of 30 Å of aluminum is oxidized. The zero-field energy gap (b) decreases with thickness and depends strongly on the base pressure of the deposition chamber. Some values of $T_c$ as calculated with equation (10.4) are included. The right-hand axis indicates the corresponding critical field.

Usually the base pressure of the chamber is in the low $10^{-8}$ mbar range. Under these conditions, a $T_c$ of about 1.9 K and a critical field of 3.5 T can be obtained with an as-deposited aluminum thickness of 40 Å. Figure 10.4-(a) shows the corresponding zero-field gap and the obtainable Zeeman splitting measured at 0.3 K on a junction with a Co top
Chapter 10. The superconducting electrode

Figure 10.4: Representative conductance measurements at 0.3 K of Al/AlO\textsubscript{x}/Co junctions deposited while the base pressure was in the low 10\textsuperscript{-8} mbar range. The solid lines are theoretical fits. When the aluminum is deposited directly on the glass substrate (a), critical fields of roughly 3.5 T are obtained, while a Mg seed layer (b) results in critical fields larger than 4.5 T. With the Mg seed a better resolved Zeeman splitting can be obtained.

electrode. The quality of the zero-field gap is good as the conductance is zero at small bias and exceeds 1.75 at the energy gap edge. Both the zero-field and in-field measurements are in excellent agreement with the best fit of the theory (solid lines). The tunneling spin polarization \( P \) is clearly visible from the asymmetry in the in-field measurement. The \( T_c \)
and $B_c$ are sufficiently large to allow for an accurate extraction of $P$. The Zeeman splitting, however, is not as clearly resolved as compared to the calculated examples in section 7.3, as well as measurements published by others (see for example refs. [62] and [67]). In this respect the result of figure 10.4-(a) is not very satisfying. The conductance in between the Zeeman-split maxima does not show a clear local minimum, and, consequently, the inner two maxima appear merely as conductance plateaus. Since the critical field is 3.5 T and the applied field is only 2.25 T, one would guess that a better resolved Zeeman splitting can be obtained simply by increasing the applied field. This is not the case. When the field is increased, the distance between the two inner plateaus becomes smaller causing the conductance at zero bias to increase. Without a deep conductance minimum at zero bias, the inner two plateaus are not distinguishable.

To obtain a satisfactory result it is necessary to increase the $T_c$, which means that the structure of the aluminum film, in particular the average grain size, has to be changed. At this point it is relevant to mention which preparation methods are used and $T_c$’s are obtained by others. In contrast to the 1.9 K example considered above, Worledge and Geballe obtain a $T_c$ of about 2.4 K by room-temperature sputter-deposition in a chamber with a base pressure in the $10^{-6}$ mbar range [67, 68]. This large $T_c$ is caused by the poor base pressure of their deposition chamber, which, as discussed earlier, involves the incorporation of oxygen during deposition. This suggests that it is also possible to obtain a high $T_c$ with a cleaner deposition chamber by injecting an amount of oxygen. In the development stage of the junction preparation, however, oxygen injection was found to lead to irreproducible results and was therefore rejected. Monsma and Parkin obtain a $T_c$ of about 2 K by room-temperature sputter-deposition in a relatively clean chamber with a base pressure in the $10^{-9}$ mbar range [62]. They use aluminum alloyed with 2 % Cu or Si. The foreign atoms increase the nucleation density of the aluminum on the substrate and therefore lead to smaller grains and a higher $T_c$. Tedrow, Meservey and Moodera obtain $T_c$’s above 2.5 K [58, 60]. They evaporate aluminum on glass substrates cooled to liquid nitrogen temperature in a chamber with a base pressure in the $10^{-7}$ mbar range. This large $T_c$ might be a consequence of the combination of the deposition technique used and the low substrate temperature. A more important contribution to the enhancement of the $T_c$ might originate from the oxygen and water condensed on the substrate during the

**Table 10.1:** The effect of seed layers (3 to 5 Å thickness) on the $T_c$ and the gap quality in Al/AlO$_x$/N junctions.

<table>
<thead>
<tr>
<th>seed</th>
<th>effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>$T_c &lt; 0.3$ K</td>
</tr>
<tr>
<td>Ta</td>
<td>$T_c \approx 1.5$ K; poor gap quality</td>
</tr>
<tr>
<td>Ru</td>
<td>$T_c \approx 2.0$ K; gap quality preserved; somewhat larger $b$</td>
</tr>
<tr>
<td>Mg</td>
<td>$T_c \approx 2.5$ K; gap quality preserved; $b$ not influenced</td>
</tr>
</tbody>
</table>
cool-down period prior to the deposition.

The possibility that foreign atoms present on the substrate can enhance $T_c$, leads naturally to the idea of depositing a few angstroms of a metal prior to the aluminum deposition. This ultrathin layer will be referred to as the seed layer. In the development stage of the junction preparation, different seed layers have been used. The observed effect of these seed layers on the $T_c$ and the gap quality is discussed here. Magnetic metals are not to be used as the seed layer since their magnetism will quench the $T_c$. Also metals with a high atomic number are less suitable since they will increase the spin-orbit scattering rate. At first glance, vanadium seems a suitable candidate since it is a superconductor and its atomic number is low. The effect of 3 Å vanadium, however, is disastrous. The $T_c$ is quenched to a value below 0.3 K. This effect is caused by the oxidation of the vanadium atoms at the surface of the substrate. Thus, actually, the seed is VO$_x$ instead of V. Since most stoichiometries of VO$_x$ order magnetically at low temperature [86, 87], VO$_x$ is effective in suppressing the transition temperature. Another example in which VO$_x$ plays a role is discussed in section 10.3. A similar effect, although not as dramatic as with vanadium, is observed with tantalum. Ta is often used as a buffer layer for magnetic tunnel junctions because of its high nucleation density on oxidic substrates [78]. This high nucleation density leads to a low surface roughness of the subsequent layers. For our purpose, however, Ta is not useful since it suppresses the $T_c$ from 1.9 K to about 1.5 K and, moreover, degrades the gap quality. Apparently, like VO$_x$, also TaO$_x$ quenches the superconductor as if it were magnetic. In contrast with V and Ta, enhanced $T_c$’s with a preserved gap quality are obtained with 3 to 5 Å thick ruthenium and magnesium seed layers. Ru gives a small enhancement from 1.9 K to about 2.0 K, and Mg increases the $T_c$ significantly to about 2.5 K. Figure 10.4-(b) shows that with the Mg seed layer a clearly resolved Zeeman splitting can be obtained with pronounced local minima instead of plateaus as is the case in figure 10.4-(a). Due to its low atomic number, the Mg seed does not influence the normalized spin-orbit scattering rate $b$. Ru, however, increases $b$ with a small but noticeable amount. The effect of the different seeds are summarized in table 10.1. Probably, the effect of the Mg and Ru seed is similar to the effect of the Cu and Si doping used by Monsma and Parkin.

Summarizing, with sputter-deposition under the cleanest possible conditions, Al/AlO$_x$/N junctions can be prepared reproducibly with relatively large $T_c$, $B_c$, and good gap quality by depositing the aluminium on a 5 Å magnesium seed. The experiments described in chapter 11 and 12 are performed with Al/AlO$_x$/N junctions prepared with a Mg seed.

So far we have been considering junctions of which the superconductor is the bottom electrode, that is, the superconductor is deposited on the substrate. In the remainder of this chapter we consider junctions where the superconductor is deposited on top of the barrier.
N/barrier/Al junctions

The aluminum and the AlO_x tunnel barrier of the Al/AlO_x/N junctions considered previously are amorphous, and, as a consequence, the ferromagnetic top electrode has a polycrystalline structure. When one wants to study the tunneling spin polarization in junctions with single-crystalline ferromagnetic electrodes, or electrodes with a better defined structure, it is necessary to deposited the ferromagnetic electrode on a properly chosen substrate and, consequently, the aluminum on top of the barrier. In this configuration it has proven to be much more difficult to obtain a large enough $T_c$ and sufficient gap quality for clear observation of Zeeman splitting.

The results considered next are obtained with N/barrier/Al junctions with amorphous AlO_x and MgO barriers. The bottom electrode of the junctions consists of 40 Å Co deposited on a 20 Å Ta buffer layer. The AlO_x barriers are prepared by plasma-oxidation of a 25 Å Al film and the MgO barriers by plasma-oxidation of a 22 Å Mg film (see section 9.1). The aluminum used for the top electrodes contains 1% Cu to increase the $T_c$.

Figure 10.5-(a) shows the conductance of a Co/AlO_x/Al junction. The as-deposited thickness of the Al top electrode is 55 Å and the $T_c$ is about 1.8 K. Although in zero field the conductance at zero bias is essentially zero, the maxima at the energy gap edge are low as compared to those obtained with the Al/AlO_x/N junctions. This is possibly related to the aluminum structure and the structure of the barrier/aluminum interface which are different in this configuration. The critical field and the gap quality do not allow for observation of Zeeman splitting. If the thickness could be reduced significantly, probably the $T_c$ would be higher as is the case with deposition on glass. This is not possible, however, since already below about 45 Å the sheet conductance of the electrode is zero due to a smaller nucleation density of Al on AlO_x and probably a larger surface roughness of the amorphous AlO_x.

Figure 10.5-(b) shows Co/AlO_x/Al junctions of which the aluminum is deposited on Ru seed layers in an attempt to improve the gap and enhance the $T_c$. The trend with increasing Ru thickness is indicated by the arrows in the figure. As can be seen from the width of the gaps, the $T_c$ is not dependent on the Ru thickness. Although the Ru somewhat improves the energy gap edge maxima and reduces the zero bias conductance, it leads to unwanted additional maxima at above-gap bias voltage. The origin of the above-gap maxima is not known. The double peak structure is reminiscent of the two-gap superconductivity reported for a few single-crystalline superconductors [88, 89].

Figure 10.5-(c) shows the conductance of a Co/MgO/Al junction. With an MgO barrier the as-deposited Al thickness can be made thinner as compared to AlO_x, indicating a higher Al nucleation density or possibly a smaller surface roughness. The gap quality of this junction is the best one obtained with the N/barrier/Al configuration, however, for unknown reasons, this result could not be reproduced. The sharpness of the energy gap edge maxima is comparable to those obtained with Al/AlO_x/N junctions, and lead to a weak but observable signature of Zeeman splitting in an applied field of 2.25 T. From the asymmetry it is apparent that the tunneling polarization of this junction is smaller as compared to those of the Al/AlO_x/Co junctions shown in figure 10.4. This is most-likely
Chapter 10. The superconducting electrode

Figure 10.5: Conductance measurements at 0.3 K on junctions of which the Al electrode is deposited on top of amorphous AlO\(_{x}\) barriers (a and b) and a MgO barrier (c). A ruthenium seed layer below the aluminum (b) does not improve the gap quality satisfactorily but instead induces above-gap conductance maxima. The trend with increasing Ru thickness is indicated by the arrows.
caused by the differences in the AlO\textsubscript{x}/Co and Co/MgO interface structures.

A few spin-polarized tunneling measurements with N/barrier/Al junctions are reported by others. Here we mention two. Moodera et al. have been able to measure the tunneling polarization in N/AlO\textsubscript{x}/Al junctions with crystalline NiMnSb and Ni bottom electrodes [61, 66] prepared in a similar way as the junction preparation procedure described previously. That is, the top and bottom electrode are deposited through a metal shadow mask and the barrier is prepared by plasma oxidation of an aluminum film. One difference, however, possibly responsible for their success, is the technique used for the deposition of the aluminum electrode. Instead of sputter-deposition they used evaporation.

Measurements of the tunneling polarization in La\textsubscript{0.67}Sr\textsubscript{0.33}MnO\textsubscript{3}/SrTiO\textsubscript{3}/Al and SrRuO\textsubscript{3}/SrTiO\textsubscript{3}/Al junctions are published by Worledge and Geballe [67, 68]. The bottom electrode and the SrTiO\textsubscript{3} barrier of these junctions are epitaxially grown by pulsed-laser deposition while the aluminum top electrode is deposited by sputter-deposition. Also here the bottom and top electrodes are obtained with use of a shadow mask. In contrast to the examples considered previously, the gap quality of these N/barrier/Al junctions is excellent, even comparable to that of the Al/AlO\textsubscript{x}/Co junction shown in figure 10.4-(b). The high quality of the gap is probably a consequence of the low surface roughness of the crystalline SrTiO\textsubscript{3} barrier. Another issue involved might be the nucleation of the aluminum on the SrTiO\textsubscript{3}, which can be different from the nucleation on amorphous AlO\textsubscript{x} and MgO.

Summarizing, a preparation procedure for Al/AlO\textsubscript{x}/N junctions based on sputter-deposition and plasma oxidation has been developed leading to a reproducible and satisfactory quality. Various approaches to realize high-quality N/barrier/Al junctions, however, have been not successful.

### 10.3 Vanadium electrodes

The spin-orbit scattering rate in the superconductor used for spin-polarized tunneling should be low enough to resolve the Zeeman splitting in the superconducting density of states (see section 8.3). Therefore, only superconductors with a relatively low atomic number are suitable in principle. One of these superconductors, besides aluminum, is vanadium. Although a resolvable Zeeman splitting has been demonstrated experimentally [90], published spin-polarized tunneling studies with vanadium superconductors are rare because achieving a sufficient gap quality has proven to be much more difficult as compared to aluminum. The results reported below suggest that a poor gap quality and suppression of \(T_c\) with a vanadium superconducting electrode is attributable to oxygen impurities, in contrast to the case of aluminum where oxygen impurities are enhancing the \(T_c\).

The bottom electrode of the junctions consists of 30 Å Co deposited on a 20 Å Ta buffer layer, and the tunnel barrier is obtained by plasma-oxidation of 25 Å Al. Vanadium top electrodes are deposited with a deposition rate of 0.5 Å/s and 2.0 Å/s. The vanadium has a thickness of 250 Å and is capped with 30 Å Al. Figure 10.6 shows the conductance at 0.3 K obtained with both deposition rates. The energy gap of the vanadium electrode deposited with 2.0 Å/s is significantly larger than the one obtained with 0.5 Å/s. According
to equation (10.4), the corresponding transition temperatures are 4.0 K and 3.3 K for the high and low deposition rate, respectively. The $T_c$ of pure bulk vanadium is 5.4 K [29]. The critical field of the vanadium electrode deposited with 2.0 Å/s is measured to be about 3.5 T. The combination of the limited gap quality and the limited critical field prevents observation of Zeeman splitting.

The dependence on the deposition rate is a strong indication that the suppression of $T_c$ originates from the partial oxygen pressure in the deposition chamber. The amount of incorporated oxygen increases with the deposition time, and is therefore lower in the electrode deposited with the higher deposition rate. The amount of incorporated oxygen can be estimated to be several percent (see section 9.1). It is observed earlier that these oxygen amounts have significant influence on the $T_c$ of vanadium films [91]. The strong sensitivity for oxygen is due to the magnetic ordering of VO$_x$ at low temperature, as mentioned earlier in section 10.2. The oxygen atoms form bonds with vanadium and therefore act as magnetic impurities effectively suppressing the transition temperature.

We can see from figure 10.6 that not only the width of the energy gap depends on the deposition rate, but also the quality of the gap. The faster deposition results in a

![Figure 10.6: Conductance of Co/AlO$_x$/V(250Å) tunnel junctions measured in zero magnetic field at 0.3 K. The quality of the superconducting energy gap and the transition temperature depend on the vanadium deposition rate. The dependence can be explained by the finite partial oxygen pressure in the deposition chamber during deposition.](image)

117
better gap quality, i.e. the conductance at zero bias is lower and the conductance maxima at the energy gap edge are higher. In general, the most simple explanation for a finite conductance at zero bias are metallic pinholes in the tunnel barrier. Here, however, the zero bias conductance depends on the deposition rate of the superconductor, which strongly suggests that the finite zero bias conductance is not due to metallic pinholes in the barrier but instead originates from the oxygen impurities. Apparently, the oxygen atoms perturb the BCS density of states leading to a finite density of states at the Fermi level and rounded maxima at the energy gap edge. This perturbation is similar to the one induced by depairing as discussed earlier in section 8.3.

In summary, the major disadvantageous property of vanadium over aluminium is the strong sensitivity for oxygen impurities. Due to the magnetic nature of the vanadium-oxides, the oxygen impurities act as magnetic impurities effective in suppressing the $T_c$ and degrading the gap quality. We have argued that a finite conductance at zero bias is not always caused by metallic pinholes in the tunnel barrier, but can instead originate from a finite density of states at the Fermi level in the superconductor.
Chapter 11

Barrier dependence of tunneling spin polarization

The topic of this chapter is the dependence of the tunneling spin polarization on the barrier material. To investigate this dependence, the tunneling spin polarization in Al/barrier/ferromagnet junctions is measured for a given ferromagnet with different amorphous barrier materials. As for the junctions with AlO$_x$ barriers, good gap quality and clear Zeeman splitting is obtained with MgO barriers. The polarization found with MgO is significantly different as compared to those obtained with AlO$_x$. Furthermore, it is shown that clear Zeeman splitting is in principle difficult to obtain with the heavy metal oxide barriers TaO$_x$ and HfO$_x$, due to a large spin-orbit scattering rate in the superconductor induced by heavy Ta and Hf atoms most likely present at the Al/barrier interface.

Parts of the work described here have been published in Physical Review B [63] and in IEEE Transactions on Magnetics [92].

11.1 Introduction

Recently, experimental TMR results have suggested that the sign and magnitude of the tunneling spin polarization depends on the choice of the material used for the tunnel barrier. For example, in contrast with the positive TMR effect found with AlO$_x$ barriers [58], De Teresa et al. have shown that the TMR in La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrTiO$_3$/Co junctions is negative [72]. The negative TMR is explained by a negative $P$ of the electrons tunneling from the Co electrode.

Such experimental results and various theoretical calculations (see for example ref. [70, 71]), have cumulated into a hypothesis that can be summarized by the simple rule of thumb shown by table 11.1: Barriers that contain $d$-orbitals (such as SrTiO$_3$, TaO$_x$ and HfO$_x$ [93]) favor tunneling of electrons with $d$-character, while barriers without $d$-orbitals (such as AlO$_x$ and MgO) favor tunneling of electrons with $s$-character. The rule predicts that in a junction with a Co electrode a negative $P$ is to be expected with SrTiO$_3$, TaO$_x$ and HfO$_x$ barriers, since the polarization of the density of states of the $d$-electrons at the
Fermi level in Co is negative (see section 1.2).

The barrier dependence of the tunneling spin polarization originates from the spin dependence of the tunnel probability as introduced in section 1.2. Here we discuss a simplified explanation for the spin dependence of the tunnel probability in terms of a free electron picture. Consider the energy diagrams shown in figure 11.1. The tunnel probability is extremely sensitive to the effective barrier height experienced by the electrons, which is in turn determined by the bottom of the conduction band in the insulator. The effective barrier height experienced by a spin-up electron can be different from that of a spin-down electron.

The barrier height can be different in two ways. The bottom of the conduction band can be exchange-split as is the case in some magnetic insulators [94, 95]. Such tunnel barriers are referred to as spin filters and will not be considered here. The other source of a spin-dependent barrier height, of importance in non-magnetic insulators, originates from a character difference of the spin-up and spin-down electrons at the Fermi level. Consider, for example, the interfacial density of states diagram of the ferromagnetic electrode shown in figure 11.1. The spin-up DOS is drawn to depend strongly on energy in the vicinity of the Fermi level, while the spin-down DOS at the Fermi level has a weaker energy dependence. This reflects that the spin-up electrons have predominantly a $d$-character and the spin-down electrons predominantly an $s$-character (see section 1.2). Due to this character difference, the barrier height experienced by the spin-up electrons is different from that of the spin-down electrons since the overlap of the electron wave-function with the states at the bottom of the conduction band in the insulator is different. For example, when the bottom of the conduction band is composed of $d$-character states and $s$-character states are located at somewhat higher energy (which is the case in HfO$_2$, [70, 93]), the overlap between the $s$-character electrons at the Fermi level and the $d$-states at the bottom of the conduction band will be relatively small. Consequently, the barrier height experienced by the tunneling $s$-character electrons will be larger than that of the $d$-character electrons so that tunneling of $d$-character electrons is favored.
Chapter 11. Barrier dependence of tunneling spin polarization

![Diagram of a tunnel junction with corresponding energy diagrams.](image)

**Figure 11.1:** Tunnel junction with corresponding energy diagrams.

**Motivation**

To date, the role of the barrier material is studied experimentally only with TMR experiments, which, however, give indirect indications of the tunneling polarization (see section 1.2). Direct spin-polarized tunneling investigations addressing the barrier dependence are lacking. Though, a few spin-polarized tunneling measurements on junctions with tunnel barriers other than amorphous AlO$_x$ have been reported. Worledge and Geballe used SrTiO$_3$ barriers to measure $P$ in La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrTiO$_3$/Al and SrRuO$_3$/SrTiO$_3$/Al junctions [67, 68]. Parker *et al.* have measured CrO$_2$/Cr$_2$O$_3$/Al junctions [69]. To date, the spin-polarized tunneling technique has not been used to systematically investigate the barrier dependence of $P$ by comparing junctions with a given fixed ferromagnetic electrode and different barriers.

In the remainder of this chapter a spin-polarized tunneling study is presented addressing junctions with various barrier materials. First, junctions with AlO$_x$ and MgO barriers are considered, thereafter results obtained with TaO$_x$ and HfO$_x$ are discussed.
11.2 AlO$_x$ and MgO barriers

Al/AlO$_x$/Co and Al/AlO$_x$/Fe junctions are prepared as described in section 9.1. The AlO$_x$ junctions have a resistance of about 1 kΩ ($10^5$ kΩµm$^2$ resistance-area product) with roughly a 50 % resistance increase upon cooling. This temperature dependence is usually obtained with amorphous AlO$_x$ [96] and indicates that single-step tunneling is the dominant conduction mechanism. Figure 11.2-(a) shows a representative measurement of an Al/AlO$_x$/Co junction. The polarization is extracted by fitting the theory described in chapter 8. This theory accounts for the effect of orbital-depairing and spin-orbit scattering on the superconducting density of states. A tunneling spin polarization of $+39 \pm 1 \%$ and $+41 \pm 1 \%$ is found with Co and Fe top electrodes, respectively. The error margins in this result are determined by sample-to-sample variation. The tunneling polarizations and the values found for the depairing and spin-orbit scattering parameters are in agreement with earlier work [60, 62].

To study the barrier dependence of $P$, the AlO$_x$ barrier is replaced by MgO. The junctions with MgO barriers are prepared as follows. First, a superconducting Al bottom electrode with a thickness of 20 Å is deposited. Then the entire substrate is covered by an Mg film with a thickness varied between 20 and 25 Å (see section 9.1). Subsequently, the Mg film is exposed to an oxygen plasma with the same fixed parameters as used for the AlO$_x$ junctions, and finally Co or Fe top electrodes are deposited. The limited Mg thickness window of 20-25 Å is not arbitrary. Mg thicknesses less than 20 Å result in Al bottom electrodes with a high resistivity due to severe over-oxidation. Mg thicknesses larger than 25 Å cannot be used since for the parameters used, the oxidation of the Mg films is self-limited to 25 Å.

The barrier structure of the MgO junctions is characterized with in-situ angle-resolved X-ray photo-electron spectroscopy (XPS) (see section 9.4). Spectra can be measured with the sample surface perpendicular to the spectrometer (referred to as “normal emission”) and with the sample surface under grazing angle with respect to the spectrometer (referred to as “grazing emission”). By comparing the normal and grazing emission spectra depth resolution is obtained since in the grazing emission spectra the XPS intensity from atoms below the surface is suppressed. Figure 11.3-(a) shows the XPS spectra of the Al 2$p$ and Mg 2$p$ region measured on an Al(20 Å)/Mg(23 Å) bilayer before the oxygen plasma exposure. Part of the Mg intensity shows a chemical shift since some Mg is oxidized. This is most visible in the grazing emission spectrum since the MgO is located at the surface. This MgO is formed due to the finite partial oxygen pressure in the vacuum system in combination with the high chemical reactivity of Mg. The ratio between Al and Mg intensity is significantly smaller in the grazing emission spectrum. This implies that Mg is located at the surface, which rules out severe intermixing with Al during deposition. Figure 11.3-(b) shows the normal and grazing emission spectra measured after exposure to the oxygen plasma. The Mg intensity shows a complete chemical shift from which it can be concluded that all Mg is oxidized. However, also part of the Al intensity is shifted reflecting the presence of oxidized Al. That is, for this thickness of the Mg film the barrier
of the MgO junctions contains an amount of oxidized Al. The ratio between the intensity from the oxidized Al and Mg is smaller in the grazing emission spectrum, which shows that after the plasma oxidation the MgO is still predominantly located at the surface. The dependence of the Al-Mg ratio on the angle of the sample surface in this case, however, is
less pronounced as compared to before the plasma oxidation. This indicates that at the Al/MgO interface a certain amount of AlO$_x$ is intermixed with MgO.

From the XPS measurements discussed above it can be concluded that at the Al/MgO interface an amount of AlO$_x$ is intermixed with MgO. This AlO$_x$ amount is largest in the MgO junctions prepared with 20 Å Mg thickness. The junction resistance-area product increases with AlO$_x$ amount from roughly $10^3$ kΩµm$^2$ for the junctions prepared with 25 Å Mg films, to $10^5$ kΩµm$^2$ with 20 Å Mg films. This is consistent with the higher barrier height for tunneling of AlO$_x$ as compared to MgO (2-3 eV versus 1 eV [96, 97]). Thus, by varying the Mg film thickness, we vary the amount of AlO$_x$ intermixed with MgO at the Al/MgO interface, and the junction resistance varies over orders of magnitude accordingly.

![Figure 11.3: In-situ XPS (Al K$_\alpha$) on the 20 Å Al bottom electrode covered with a 23 Å Mg film before (a) and after (b) the plasma oxidation. See text for details.](image-url)
Chapter 11. Barrier dependence of tunneling spin polarization

Table 11.2: Overview of results.

<table>
<thead>
<tr>
<th>junction</th>
<th>$P$</th>
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<tbody>
<tr>
<td>Al/AlO$_x$/Co</td>
<td>$+39 \pm 1 %$</td>
</tr>
<tr>
<td>Al/AlO$_x$/Fe</td>
<td>$+41 \pm 1 %$</td>
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<tr>
<td>Al/MgO/Co</td>
<td>$+30 \pm 2 %$</td>
</tr>
<tr>
<td>Al/MgO/Fe</td>
<td>$+30 \pm 2 %$</td>
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</table>

The resistance increase of the MgO junctions during cooling is about 50 %, similar to the AlO$_x$ junctions, which indicates that also in these junctions single-step tunneling is the dominant conduction mechanism. Figure 11.2-(b) shows a representative conductance measurement of an Al/MgO/Fe junction. As for the AlO$_x$ junctions, high-quality superconducting gaps with sharp maxima at the energy gap edge are obtained, and the in-field measurement shows clear zeeman splitting. From the fits we extract a tunneling spin polarization of $+30 \pm 2 \%$ for both junctions with Fe and Co top electrodes. Interestingly, within the experimental accuracy, $P$ is independent of the AlO$_x$ amount and junction resistance. This means that the AlO$_x$ amount present at the Al/MgO interface, has no significant influence on the tunneling polarization.

Since the polarization of the density of states of the $s$-electrons at the Fermi level in Co and Fe is positive, the positive sign of $P$ in the MgO junctions indicates that tunneling is dominated by $s$-electrons, which is consistent with table 11.1. The magnitude of $P$ obtained with the MgO junctions is significantly different as compared to the AlO$_x$ junctions (see table 11.2). This dependence can be brought about by the intrinsic electronic interface structure, but possibly also extrinsic effects can obscure the interpretation of the results. In the next paragraphs a more detailed analysis is used to exclude the most plausible extrinsic effects.

As mentioned by Monsma and Parkin [98], one complication can be the oxidation of the ferromagnet at the barrier/ferromagnet interface. At low temperature, this oxide orders anti-ferromagnetically and prevents proper magnetization of the ferromagnet at the interface leading to a loss of tunneling spin polarization. This mechanism plays a role in magnetic tunnel junctions with anti-ferromagnetic barriers such as NiO and CoO where only relatively small TMR effects are obtained [60]. The oxidation state of the ferromagnet in the present junctions is studied with in-situ XPS. For careful investigation of the barrier/ferromagnet interface, samples are used of which the thickness of the ferromagnetic electrode deposited on top of the barrier is only 4 Å. As an example, the case of Fe on MgO is considered here. Figure 11.4 shows the Fe 2$p$ lines measured immediately after deposition (as-deposited) and, for comparison, after an exposure to oxygen. The spectrum measured after the deliberate oxidation shows a clear chemical shift of about 5 eV. This proves that at the as-deposited interface FeO$_x$ is absent. In this way oxidation of the ferromagnet in all the AlO$_x$ and MgO junctions is excluded.
Another mechanism leading to loss of tunneling spin polarization is spin-orbit scattering at the barrier/ferromagnet interface due to the combination of spin-orbit interaction and a degree of disorder. This mechanism may explain the relatively small TMR effects obtained with the heavy metal oxides TaO$_x$ and HfO$_x$ [99, 100]. It cannot explain, however, the lower polarization found with the MgO barrier since the atomic number of Mg is smaller than that of Al. Apparently, in the present AlO$_x$ and MgO junctions spin-orbit scattering is not important. The above arguments substantiate that the observed difference in the tunneling spin polarization in the AlO$_x$ and MgO junctions is intrinsically determined by the barrier material.

Recently, measurements on epitaxial Fe/MgO/Fe junctions have shown a large TMR effect [101, 102]. From this TMR a tunneling polarization can be estimated using the Julliere formula (see section 1.2). This polarization, which we denote as the Julliere polarization, is roughly 50 to 60%. From calculated TMR magnitudes in epitaxial Fe/MgO/Fe junctions [103, 104], even higher values for the Julliere polarizations can be estimated. These Julliere polarizations, however, cannot be compared directly with the polarization of 30% measured here since this polarization is found for an amorphous MgO barrier. An amorphous barrier certainly leads to a different electronic interface structure as compared to an epitaxial barrier. Furthermore, it is believed that the absence of the conservation of the momentum in parallel with the barrier during tunneling through amorphous barriers, leads to an averaging of spin-polarized currents in different crystallographic orientations. This possibly reduces the effective tunneling spin polarization. A detailed theoretical understanding of $P$ in amorphous junctions which addresses this issue in full detail is currently not available.

**Figure 11.4:** *In-situ* XPS (Al K$_\alpha$) measurements of Fe at the MgO/Fe interface. From the measurements it can be concluded that the Fe at the interface is not oxidized.
11.3 TaO$_x$ and HfO$_x$ barriers

To investigate the sign and magnitude of the tunneling polarization in junctions with a barrier containing $d$-orbitals, attempts are made to realize suitable junctions with TaO$_x$ and HfO$_x$ barriers. The quality of the junctions, however, is insufficient for extraction of the tunneling polarization due to difficulties explained below. First the TaO$_x$ junctions will be discussed and after that the HfO$_x$ junctions.

The TaO$_x$ junctions are prepared in the same way as the MgO junctions. Like Al and Mg, the oxidation of Ta films is self-limited. The oxygen plasma exposure used for the barrier formation is able to completely oxidize Ta films with a thickness of 15 Å. The TaO$_x$ junctions have a resistance of roughly 10 Ω at room temperature ($10^3$ kΩ µm$^2$) and 100 Ω at low temperature. This large increase of the junction resistance during cool down indicates a thermally activated conductance mechanism in the TaO$_x$, in contrast with the desired single-step tunneling. Figure 11.5-(a) shows a representative measurement of an Al/TaO$_x$/Co junction in zero field, and an in-plane field of 4 T. The gap quality is poor as compared to the AlO$_x$ and MgO junctions. The finite conductance at zero bias and the relatively weak peaks at the energy gap edge may be related to the thermally activated conductance mechanism. The energy gap corresponds to a $T_c$ of about 1.1 K, in sharp contrast with 2.2 K obtained with the other junctions.

The critical field of ultra-thin superconducting Al is limited by Pauli spin paramagnetism as explained in section 10.1. Accordingly, the critical field in Tesla is roughly given by twice the transition temperature in Kelvin (equation (10.5)). The critical field of 4 T and transition temperature of 2.2 K found for the AlO$_x$ and MgO junctions are in nice agreement with this relation. In contrast, the critical field found for the TaO$_x$ junction is larger than 4 T while the transition temperature corresponding to the energy gap is only 1.1 K, significantly smaller than the 2.2 K one would expect. Probably, the observed energy gap is in some way suppressed by intermixing of Ta with Al during the plasma oxidation of the Al/Ta bilayer, meaning that there are Ta atoms present in the superconducting electrode. If this is the case, then the Ta atoms induce a high spin-orbit scattering rate due to their large atomic number and, consequently, Zeeman splitting will be quenched. The measurement performed in a field of 4 T, which shows no sign of Zeeman splitting, is consistent with this picture.

In general, intermixing of the bottom electrode and barrier film during plasma oxidation is a complication inherent to the preparation procedure, and occurs or may not occur depending on the choice of the elements used. Possibly the ratio between the chemical reactivity of the elements plays a role in the oxidation dynamics. The success obtained with the MgO junctions described previously can be due to the high chemical reactivity of Mg as compared to Al, meaning that MgO is stable against Al (see table 9.1). On the other hand, the reactivity of Al is larger than that of Ta. The ability of Al to "steal" oxygen from TaO$_x$ might be a driving force for intermixture.

After the TaO$_x$ junctions, attempts were made to make suitable junctions with HfO$_x$. The reactivity of Hf is larger than that of Al, meaning that HfO$_x$ is stable against Al. Here
we consider a junction of which the preparation differs only from that of an $\text{AlO}_x$ junction by the deposition of two mono-layers Hf on top of the Al electrode prior to the oxygen plasma exposure. Ideally, in absence of intermixing, this would result in an $\text{Al}/\text{AlO}_x/\text{HfO}_x/\text{Co(Fe)}$ junction. This structure, however, is not obtained. Figure 11.5-(b) shows that in zero field the conductance has the required sharp maxima at the energy gap.

**Figure 11.5:** Conductance measurements at 0.3 K of an $\text{Al}/\text{TaO}_x/\text{Co}$ junction (a), and an $\text{Al}/\text{AlO}_x/\text{Co}$ junction with HfO$_x$ in the barrier (b). The measurements are performed in zero field and an in-plane field of several Tesla. The solid lines are theoretical fits.
edge similar to the gaps shown in figure 11.2-(a). In an applied field, however, the Zeeman splitting cannot be observed clearly due to an increased spin-orbit scattering rate preventing precise extraction of $P$. From the model fit a positive polarization can be identified and a spin-orbit scattering time $\tau_{so}$ of about 1 ps can be deduced. This $\tau_{so}$ is roughly 40 times lower than obtained for the clean Al/AlO$_x$ case. The increased spin-orbit scattering rate in the Al is induced by the Hf atoms which, like Ta, have a relatively large atomic number (72 and 73 for Hf and Ta, respectively). It has been observed earlier that Zeeman splitting is quenched due to a high spin-orbit scattering rate induced by an amount of heavy impurities present in the Al electrode [58]. Apparently, the electron system of the Al bottom electrode is in direct contact with heavy Hf atoms. This means that, as a result of intermixture, Hf atoms, in view of there high reactivity most likely bond to oxygen, are located at the Al/AlO$_x$ interface. In other words, the obtained barrier is a mixture of AlO$_x$ and HfO$_x$.

The results discussed here imply that, apart from the problem of intermixture, it is in principle not possible to observe clear Zeeman splitting in Al/HfO$_x$/ferromagnet and Al/TaO$_x$/ferromagnet junctions due to the induced additional spin-orbit scattering originating from the large atomic numbers of Hf and Ta (72 and 73, respectively). This is not an issue with MgO since the atomic number of Mg is 12, one lower than that of Al.

### 11.4 Conclusions and suggestions

A significant difference in the tunneling spin polarization in junctions with AlO$_x$ and MgO barriers is observed. Observations indicate that the difference is intrinsically determined by the barrier material. With both Co and Fe as the ferromagnetic electrode, the tunneling spin polarization is roughly +40% in the AlO$_x$ junctions and +30% in the MgO junctions. This positive sign is consistent with the belief that in absence of $d$-orbitals in the barrier material, tunneling is dominated by electrons with $s$-character.

It is in principle not possible to observe clear Zeeman splitting in Al/HfO$_x$/N and Al/TaO$_x$/N junctions due to the large spin-orbit scattering rate induced by the heavy Hf and Ta atoms at the Al/barrier interface.

Worledge and Geballe have reported clear Zeeman splitting obtained with junctions of which the Al electrode is deposited on an epitaxial SrTiO$_3$ barrier [67, 68]. Apparently, the atomic number of Sr (38), which is considerably smaller than those of Hf and Ta (72 and 73, respectively), is not inducing a significant increase in the spin-orbit scattering rate. This implies that clear observation of Zeeman splitting can be obtained with Al/SrTiO$_3$/Co and Al/SrTiO$_3$/Fe junctions, enabling a direct comparison between the polarization. Conclusive direct evidence of the decisive role of the barrier for the character of the tunneling electrons, would be the observation of a negative polarization in the Al/SrTiO$_3$/Co junction and a positive polarization in the Al/SrTiO$_3$/Fe junction.
Chapter 12

Thermal stability of tunneling spin polarization

This chapter describes a unique and technologically relevant spin-polarized tunneling study of the thermal stability of the tunneling spin polarization. Parts of the work have been published in Applied Physics Letters [105], Journal of Magnetism and Magnetic Materials [106], and in Journal of Applied Physics [107].

12.1 Motivation

Because of their large room-temperature tunnel magnetoresistance (TMR) effect and their favorable resistance, magnetic tunnel junctions are considered to be suitable as the storage elements of a non-volatile magnetic random access memory (MRAM) (see section 1.1). The development of TMR-based MRAM requires incorporation of tunnel junctions into existing semiconductor technology [6]. Back-end processing in complementary metal-oxide-semiconductor (CMOS) technology involves heat treatment steps with temperatures around 400 °C. The junctions and their TMR effect, are therefore required to be thermally stable against temperatures as high as 400 °C. However, when tunnel junctions are exposed to post-deposition anneals, a severe collapse of the TMR above 300 °C is observed. An example of the dependence of TMR on anneal temperature is shown in figure 12.1. The data is obtained with Co$_{82}$Fe$_{18}$/AlO$_x$/Co$_{82}$Fe$_{18}$/Ir$_{26}$Mn$_{74}$ junctions by Cardoso et al. [108], and is representative for comparable junctions studied by others. Due to its implications on the development of MRAM, the origin of the collapse has become a main topic in the current field of research on magnetic tunnel junctions (see for example refs. [108–112]). Despite the large research effort, however, the origin of the collapse is unknown to date.

In addition to the collapse above 300 °C, figure 12.1 shows that anneals below 250 °C considerably enhance the TMR. The enhancement will be briefly addressed in the next section.

The junctions studied by Cardoso et al. are an example of state-of-the-art AlO$_x$-based magnetic tunnel junctions. The material used for the electrodes is a CoFe alloy with an
Fe content between 10 and 20 atomic percent. With optimized preparation procedures, this material has proven to give the largest TMR effects. To achieve the antiparallel state, the magnetization of the bottom or the top CoFe electrode is exchange biased, or “pinned”, by an adjacent antiferromagnetic Mn alloy layer [113]. In the case of the junctions studied by Cardoso et al., the top CoFe electrode is exchange biased by an Ir$_{26}$Mn$_{74}$ layer. Instead of IrMn, also FeMn or PtMn layers are used. It is experimentally established that above 300 °C Mn atoms diffuse out of the antiferromagnetic layer through the pinned ferromagnet to the barrier interface. Since the atomic and electronic structure of the barrier interfaces are known to determine the magnitude of the TMR effect [70, 71, 114–116], and since the onset temperature of Mn diffusion coincides with the onset of the TMR collapse, it is believed that the diffusion of the Mn atoms to the barrier interface is the main cause of the collapse [108–112].

To date, investigations of the collapse are conducted solely through observations of the TMR effect. The parameter responsible for the TMR effect, however, is the tunneling spin polarization (see section 1.2). A study of the thermal stability of the tunneling spin polarization, therefore, provides valuable complementary information to the search for the origin of the TMR collapse. In the work described here, the spin polarized tunneling technique

Figure 12.1: Representative dependence of the room-temperature TMR on post-deposition annealing. The data is obtained by Cardoso et al. from Co$_{82}$Fe$_{18}$/AlO$_x$/Co$_{82}$Fe$_{18}$/Ir$_{26}$Mn$_{74}$ junctions [108].
is used to investigate the thermal stability of the tunneling spin polarization. To be able to directly address the role of Mn diffusion, Al/AlO$_x$/Co and Al/AlO$_x$/Co$_{90}$Fe$_{10}$ junctions are annealed and measured both with and without an extra Fe$_{50}$Mn$_{50}$ layer deposited on top of the ferromagnetic electrode. First the results obtained without the extra FeMn layer are discussed.

### 12.2 Intrinsic thermal robustness

To investigate the intrinsic thermal stability of the tunneling spin polarization in junctions with AlO$_x$ barriers and Co(Fe) electrodes, Al/AlO$_x$/Co and Al/AlO$_x$/Co$_{90}$Fe$_{10}$ junctions are prepared with 200 Å thick top electrodes capped with 60 Å Ta. The Co$_{90}$Fe$_{10}$ electrodes are deposited with use of a Co$_{90}$Fe$_{10}$ sputter target. Figure 12.2 shows representative spin-polarized tunneling measurements of both junctions. The tunneling spin polarization $P$ is extracted by a fit of the model described in chapter 8. The extracted $P$ is 38 ± 1 % in the junctions with Co electrodes and 48 ± 1 % in the junctions with Co$_{90}$Fe$_{10}$ electrodes. The accuracy is determined by sample-to-sample variation. The polarizations are in fair agreement with earlier work [60, 62].

**Figure 12.2:** Conductance of an Al/AlO$_x$/Co (a) and an Al/AlO$_x$/Co$_{90}$Fe$_{10}$ junction (b) at 0.3 K in zero-field and an applied field of several Tesla. The solid lines are theoretical fits.
Figure 12.3: Tunneling spin polarization in Al/AlOₓ/Co and Al/AlOₓ/Co₉₀Fe₁₀ junctions measured after a 30 minute anneal in argon atmosphere (a) and a high-vacuum chamber (b).

The junctions are post-deposition annealed for 30 minutes under Ar atmosphere, as well as in a high-vacuum chamber. The Ar atmosphere contains a partial O₂ and H₂O pressure of 10⁻² mbar, while in the high-vacuum chamber the pressure during the anneal is in the 10⁻⁹ mbar range. When annealing is performed at temperatures exceeding 500 °C, the junctions start to show metallic shorts. The shorts are probably caused by stresses in the AlOₓ barrier induced by the thermal expansion of the electrodes. Such processes are, however, not relevant for our objectives and from hereon we will only consider anneal temperatures up to 500 °C. Figure 12.3 shows the polarization as a function of anneal temperature. During the Ar anneal, all the junction parameters, such as junction resistance and the superconducting parameters, are not significantly affected, while, remarkably, the tunneling spin polarization degrades severely above 250 °C. On the other hand, under the conditions of the high-vacuum anneal, all the junction parameters including the tunneling spin polarization are stable up to 500 °C.

These results demonstrate the crucial importance of sufficiently clean annealing conditions, and indicate that the tunneling spin polarization is a delicate junction parameter. The exact origin of the degradation during the Ar anneal is unclear. At first glance, one could attribute the degradation simply to the diffusion of Ta atoms from the capping layer to the AlOₓ barrier where they affect the electronic interface structure. This can be ruled out, however, since the degradation is not observed with the high-vacuum anneal. Probably, not the capping layer itself but impurities from the Ar atmosphere are diffusing...
Chapter 12. Thermal stability of tunneling spin polarization

through the capping layer into the junction. The similarity with the onset temperature of the observed TMR collapse suggests that impurities other than Mn can be responsible for the degradation of TMR.

The stability of the tunneling spin polarization also has an implication for the speculation on the origin of the TMR enhancement, which is obtained with anneals below 250 °C [108, 117] (see figure 12.1). In one explanation, the enhancement is attributed to an increase in the tunneling polarization due to a change in the structure of the ferromagnet at the interface. No such increase is observed in the present junctions, however, and, therefore, we can consider this explanation to be unlikely.

**XPS stability study on the AlO$_x$/Co system**

In addition to the spin-polarized tunneling measurements, the structural and chemical thermal stability of the AlO$_x$/Co system is investigated with in-situ X-ray photoelectron spectroscopy (XPS) (see section 9.4). We have discussed a similar investigation involving MgO barriers in chapter 11.

The investigation focuses on two thermal processes, which are considered to play a role in earlier work. The first process, discussed by Monsma and Parkin, is the oxidation of the ferromagnet at the barrier interface [98] (see also section 11.2). Closely related, Sousa et al. report on an investigation of the AlO$_x$ barrier in their tunnel junction structure based on Rutherford backscattering and claim to observe a redistribution of oxygen [117].

The XPS measurements are performed on Al/AlO$_x$/Co samples with a Co thickness of only 5 Å to allow for careful investigation of the oxidation state of Co at the AlO$_x$/Co interface. Figure 12.4-(a) shows the XPS intensity in the Al 2s and the Co 3p region measured before annealing. Due to the oxidation state of the Al, the Al levels are chemically shifted with respect to the binding energies measured before the plasma oxidation (indicated by the vertical lines), in accordance with earlier work focused on the plasma oxidation of Al [78, 79]. The binding energies of the Co levels coincide with those documented for clean metallic Co. Figure 12.4-(b) shows the spectrum measured after the sample is annealed in the in-situ high-vacuum chamber at 500 °C. The Co levels are still located at their original positions, indicating that the Co is not oxidized during the anneal. It is also verified that the Co 2p levels, which give more XPS signal and are more sensitive to chemical changes, are not affected by the anneal as well. Finally, in order to check the sensitivity for oxidation, the sample is deliberately exposed to oxygen. Figure 12.4-(c) shows that the chemical shifts of the Co lines can be clearly resolved.

From these XPS results it can be concluded that Co at the AlO$_x$/Co interface does not reduce to an oxide either during deposition or a 500 °C post-deposition anneal. The chemical stability is expected from the formation energies of the involved oxides (see table 9.1), and is consistent with the stability of the tunneling spin polarization. The intrinsically stable system considered here, can be regarded as a test case and provides a basis for future research. Meta-stable systems, such as AlO$_x$/Ni [98] or possibly AlO$_x$/Gd and MgO/Gd (see table 9.1), studied with spin-polarized tunneling in combination with XPS (and/or
 ultra-violet photoelectron spectroscopy), provide the opportunity for observing interesting correlations between polarization and barrier/ferromagnet interface structure.

To investigate the issue of oxygen redistribution, as suggested by Sousa et al., also XPS spectra of the O 1s level are monitored. In a careful comparison of normal and grazing emission spectra (which provides depth resolution), taken before and after the anneal, no oxygen in different chemical environments, significant changes in the O/Al ratio, or a shift of the O 1s binding energy could be identified. To gain extra sensitivity for the O 1s level, the experiment is repeated on another sample without the Co layer. Also in this case no significant changes could be observed. Thus, in contrast with the claim of Sousa et al., no migration of oxygen in the AlO$_x$ barrier is observed.
12.3 The role of Mn diffusion

To investigate the effect of Mn diffusion on the tunneling spin polarization, Al/AlO$_x$/Co/FeMn and Al/AlO$_x$/Co$_{90}$Fe$_{10}$/FeMn junctions are annealed in the high-vacuum chamber. The FeMn layer has a thickness of 100 Å and is capped with 60 Å Ta. Before conclusions from spin-polarized tunneling measurements can be drawn, however, it is necessary to proof that during annealing of these junctions, Mn diffuses through the 200 Å ferromagnetic layer to the interface with the AlO$_x$ barrier. This proof is provided by in-situ XPS measurements on identically prepared junctions which have an additional 200 Å Co layer deposited on top of the FeMn layer as shown in figure 12.5. Since the Co layers are much thicker than the scale of any electronic screening lengths involved (several Å), the role of electrical fields in the Mn diffusion is negligible. The diffusion, therefore, is driven essentially only by the gradient of the Mn concentration, and can considered to be isotropic. Consequently, when Mn atoms diffuse downwards to the interface with the AlO$_x$ barrier, then, and only then, Mn atoms are also diffusing upwards through the top Co layer. The diffusion of Mn through the top Co layer can be unambiguously detected since the escape depth of the photoelectrons probed with XPS is roughly ten times smaller than the Co thickness.

Figure 12.6-(a) shows the spectra in the region of the Mn 2p levels taken from the as-deposited sample and after a 500 °C post-deposition anneal. As-deposited, no Mn can be detected, while after the anneal a huge intensity from the Mn 2p levels is present. Figure 12.6-(b) shows the corresponding spectra in the region where the 3s and 3p levels of both Mn and Co are located. Also in this region the Mn levels can be observed only

![XPS experiment for the confirmation of Mn diffusion in Al/AlO$_x$/Co/FeMn junctions.](image-url)
Figure 12.6: In-situ XPS spectra from .../FeMn/Co(200Å) in the energy region of the Mn 2p levels (a) and the 3s and 3p levels of Co and Mn (b). The spectra confirm the diffusion of Mn in the Al/AlOₓ/Co/FeMn junctions.

... after the anneal. The appearance of the Mn levels is accompanied by a decrease in the Co intensity consistent with the diffusion of Mn atoms to the surface.

The XPS measurements proof that during the anneal a significant amount of Mn diffuses through the 200 Å thick ferromagnetic electrode, which implies that Mn atoms are diffusing to the interface with the AlOₓ barrier. In addition to the Mn levels, the intensity at the Fe levels is monitored to check whether possibly also Fe atoms are diffusing. No Fe intensity could be detected convincingly, meaning that essentially only Mn atoms are diffusing.

The experiment is repeated at different temperatures to determine the onset temperature of the Mn diffusion. Figure 12.7 shows the ratio between the 2p level intensity of Mn and Co as a function of anneal temperature. Consistent with earlier investigations with Rutherford backscattering [108, 109, 117], and, as mentioned earlier, coincident with the onset temperature of the TMR collapse, the Mn diffusion starts around 300 °C.

The results of the spin-polarized tunneling measurements on the junctions with the extra FeMn layer are shown in Figure 12.8 (black markers). For comparison, the data obtained from the junctions without the extra FeMn layer (open markers) are included. Surprisingly, the tunneling spin polarization in both the junctions with and without the extra FeMn layer is stable up to 500 °C. Thus, contrary to our expectation, the diffusion
Chapter 12. Thermal stability of tunneling spin polarization

![Graph](image)

**Figure 12.7:** Mn/Co intensity ratio as a function of anneal temperature. The ratio is determined from the $2p$ levels.

of Mn to the interface with the AlO$_x$ barrier has no measurable effect on the tunneling spin polarization. At this point it is relevant to refer to earlier work of Kim and Moodera [118], who measured the tunneling polarization in comparable junctions with CoMn alloy top electrodes deposited using co-evaporation. From their results it can be concluded that Mn concentrations as high as 30 % have only a weak negative effect on the tunneling polarization, which is consistent with the results presented here.

![Graph](image)

**Figure 12.8:** Tunneling spin polarization in Al/AlO$_x$/Co and Al/AlO$_x$/Co$_{90}$Fe$_{10}$ junctions measured after a 30-minute post-deposition high-vacuum anneal. The polarization in the junctions with the FeMn layer on top of the ferromagnet (black markers) is not affected by the Mn diffusion.
12.4 Conclusions and suggestions

In conclusion, the investigated Al/AlO$_x$/Co and Al/AlO$_x$/Co$_{90}$Fe$_{10}$ junctions, including their tunneling spin polarization, are intrinsically stable up to 500 °C. The tunneling spin polarization appears to be the most vulnerable junction parameter and is preserved only when annealing is performed under sufficiently clean conditions. Under less clean conditions, the tunneling spin polarization degrades severely above 250 °C, similar to the collapse of the TMR observed in comparable junctions. This degradation is attributable to impurities diffusing from the environment into the junctions. The diffusion of Mn atoms to the AlO$_x$ barrier interface in Al/AlO$_x$/Co/FeMn and Al/AlO$_x$/Co$_{90}$Fe$_{10}$/FeMn junctions is confirmed. In contrast with the current believe, the Mn diffusion has no observable effect on the tunneling spin polarization. The results presented here suggest that a thermally robust TMR effect up to 500 °C is achievable in principle.

To clarify the apparent contradiction between the thermally robust tunneling spin polarization described here and the observed TMR collapse, further experiments are indispensible. In the earlier work on the thermal stability of TMR [108–112], magnetic tunnel junctions are post-deposition annealed with background pressures of 10$^{-6}$ mbar or higher, while the present high-vacuum anneals are performed in the 10$^{-9}$ mbar pressure range. Surprisingly, a possible dependence of the observations on the annealing vacuum conditions is not investigated or addressed. It is demonstrated here, however, that despite the presence of a capping layer, the observed thermal behavior is dependent on the vacuum conditions during the anneal. Therefore, it cannot be excluded that the observed TMR collapse is simply due to diffusion of impurities other than Mn from the environment into the junction.
Bibliography


Summary

The topic of this thesis is the unbalance of the electron spin in currents, a parameter known as spin polarization. Spin polarization is the most important parameter within the field currently known as spintronics, and is responsible for the high magnetic field-sensitivity of modern magnetoresistive devices. In this thesis two different methods are used to measure and study spin polarization. These two methods are point contact Andreev reflection spectroscopy and spin-polarized tunneling. In both methods a superconductor serves as a detector for the spin polarization.

When a bias voltage forces electrons to flow from a normal metal (N) into a superconductor (S), the magnitude of the current is dependent on the spin polarization. This offers the opportunity to deduce the degree of spin polarization directly from the measurement of the current, or, more precisely, from the measurement of the conductance. N and S can be in metallic contact, as is the case in point contact Andreev reflection spectroscopy, or they can be separated by an ultra-thin insulator that serves as a tunnel barrier, as is the case in spin-polarized tunneling.

Since the electron transport in N/S point contacts and N/barrier/S tunnel junctions have a different nature, different physical mechanisms are responsible for the spin-dependence of the conductance. In point contacts, the spin-dependence originates from the Andreev reflection process. This is a conduction process in which two electrons with opposite spin are paired into a Cooper pair. In tunnel junctions, the spin-dependence is due to the Zeeman splitting of the spin-up and spin-down state energy in the superconductor induced by an externally applied magnetic field.

Point contacts

Point contact Andreev reflection spectroscopy is the topic of part I of this thesis. The point contacts are obtained at low temperature by pressing a superconducting tip onto a sample of the normal metal.

The conductance-voltage relation measured in case of a highly transparent N/S interface and a high polarization of the current, looks very similar to the one measured when the interface has a relatively low transparency. In chapter 3 it is pointed out that this similarity can potentially lead to a misinterpretation of the experimental data. Specifically,
the suppression of the zero-bias conductance due to a low interface transparency may be incorrectly interpreted as proof for a highly spin-polarized current.

Anomalous conductance minima at finite bias voltage observed for some contacts can be explained by a phase transition of the contact from the N/S state to the N/N state induced by the current-generated field and heating. For a series of contacts it is observed that the bias voltage at which the phase transition occurs, is systematically dependent on the contact resistance. In chapter 5 it is shown that a simple analysis of such a series can give insight in the microscopic contact geometry.

It is shown in chapter 6 that the spin polarization measured with point contact Andreev reflection spectroscopy, decays exponentially with the amount of scattering at the N/S interface. This decay is fully explained by a simple model involving spin-flip scattering in an extended interface region.

Tunnel junctions

The topic of part II of this thesis is the spin polarization of the tunnel current in S/barrier/N tunnel junctions. The polarization is measured by the well-established spin-polarized tunneling technique, also known as superconducting tunneling spectroscopy.

The junctions are prepared by a combination of room-temperature sputter-deposition and plasma oxidation. From the results presented in chapter 10, it is apparent that it is relatively difficult to prepare high-quality junctions with aluminum or vanadium superconducting electrodes deposited on top of the barrier. On the other hand, by depositing a magnesium seed prior to the deposition of aluminium, high-quality junctions with a superconducting aluminum bottom electrode are prepared reproducibly with satisfactory large transition temperature and critical field.

The topic of chapter 11 is a recently recognized aspect of spin-polarized tunneling transport, namely the dependence of the spin polarization on the insulator used for the tunnel barrier. To study this dependence, Al/barrier/Co(Fe) junctions are prepared with various barrier materials. A significant difference between the tunneling spin polarization in junctions with AlO$_x$ and MgO barriers is observed. With cobalt and iron electrodes, a tunneling spin polarization of roughly +40 % is found with an AlO$_x$ barrier and one of roughly +30 % with a MgO barrier. Observations support that this difference is intrinsically determined by the barrier material. With HfO$_x$ and TaO$_x$ barriers, the Zeeman splitting in the conductance-voltage characteristic is quenched. This is caused by the large spin-orbit scattering rate induced by the heavy hafnium and tantalum atoms that are probably located at the Al/barrier interface.

Chapter 12 describes a unique investigation of the role of manganese diffusion in the thermal stability of the tunneling spin polarization. Thermal stability is crucial for successful incorporation of tunnel junction devices into existing semiconductor technology. The diffusion of manganese is widely believed to be responsible for the collapse of the magnetoresistance effect of magnetic tunnel junctions observed above 250 °C.
Tunneling spin polarization is the parameter responsible for the magnetoresistance effect. The thermal stability of this parameter is directly investigated using the spin-polarized tunneling technique. To this end Al/AlO$_x$/Co and Al/AlO$_x$/Co$_{90}$Fe$_{10}$ junctions are used both with and without an additional FeMn layer deposited on top of the ferromagnetic electrode. The diffusion of Mn atoms from the FeMn layer to the AlO$_x$ barrier interface is confirmed independently with X-ray photoelectron spectroscopy. All the junctions, including their tunneling spin polarization, are found to be intrinsically stable up to 500 °C, showing that the diffusion of manganese has no observable influence. The tunneling spin polarization, however, is preserved only when annealing is performed under sufficiently clean conditions. Under less clean conditions, it degrades severely above 250 °C, similar as observed for the tunnel magnetoresistance effect. The degradation of the polarization is attributable to the diffusion of impurities from the environment into the junctions.
Samenvatting

Het onderwerp van dit proefschrift is het verschil in de bijdrage van spin-up en spin-down elektronen aan een elektrische stroom. Dit verschil wordt spin-polarisatie genoemd. Spin-polarisatie is verantwoordelijk voor de hoge gevoeligheid van moderne magnetoweerstandstructuren voor magneetvelden. Het proefschrift is gebaseerd op twee verschillende methoden voor het meten van spin-polarisatie. Deze methoden zijn point contact Andreev reflection spectroscopy en spin-polarized tunneling. In beide methoden fungeert een supergeleider als een detector voor de spin-polarisatie.

Wanneer een spanningsverschil wordt aangelegd tussen een normaal metaal (N) en een supergeleider (S) is de grootte van de stroom afhankelijk van de spin-polarisatie. Dit biedt de mogelijkheid om de spin-polarisatie direct te bepalen uit een meting van de stroom of, nauwkeuriger, uit een meting van de geleiding. N en S kunnen in metallisch contact zijn met elkaar of gescheiden zijn door een zeer dunne isolator die als tunnelbarrière fungeert. In het eerste geval spreekt men van een puntcontact en in het tweede geval van een tunneljunctie.

Verschillende fysische mechanismen zijn verantwoordelijk voor de specifieke relatie tussen polarisatie en geleiding omdat de aard van het elektronentransport in N/S-puntcontacten en N/barrière/S-tunneljuncties verschillend is. In puntcontacten speelt Andreev-reflectie een rol. Dit is een geleidingsproces waarbij twee elektronen met tegengestelde spin een Cooper-paar vormen. In tunneljuncties wordt de spin-afhankelijkheid veroorzaakt door de Zeeman-splitsing in de toestandsenergie van de spin-up en spin-down elektronen in de supergeleider. Hierbij is deze opsplitsing geïnduceerd door een aangelegd magnetisch veld.

Puntcontacten

Deel I van dit proefschrift gaat over point contact Andreev reflection spectroscopy. De puntcontacten zijn verkregen door bij lage temperatuur met een supergeleidende naald contact te maken met het normale metaal.

Voor een bepaald puntcontact wordt de mate van elektronen-verstrooing aan het N/S-grensvlak aangegeven met de parameter $Z$. De geleiding-spannings karakteristiek van een puntcontact met een lage $Z$ en hoge spin-polarisatie toont grote overeenkomst met die gemeten wanneer $Z$ hoog en de spin-polarisatie laag is. Zoals benadrukt in hoofdstuk 3 kan deze overeenkomst leiden tot een foutieve interpretatie van meetresultaten. De invloed
van een hoge mate van elektronen-verstrooiing op de geleiding kan onjuist geïnterpreteerd worden als een bewijs voor een stroom met hoge spin-polarisatie.

Sommige puntcontacten laten afwijkende minima zien in de geleiding bij eindige spanningen. Deze minima kunnen verklaard worden met een fase-overgang van het contact van de N/S-toestand naar de N/N-toestand. Deze fase-overgang is toe te schrijven aan een combinatie van opwarming en het magnetisch veld dat wordt gegenereerd door de stroom. Metingen aan een reeks van puntcontacten laten zien dat de spanning waarbij de fase-overgang plaatsvindt, systematisch van de weerstand van het contact afhangt. De simpele analyse in hoofdstuk 5 toont aan dat een dergelijke reeks inzicht kan geven in de microscopische geometrie van het contact.

Uit de resultaten die in hoofdstuk 6 gepresenteerd zijn blijkt dat de spin-polarisatie die gemeten wordt met point contact Andreev reflection spectroscopy exponentieel afvalt met de hoeveelheid verstrooiing aan het N/S-grensvlak. Deze afval kan volledig verklaard worden door elektronenverstrooiing in een eindig gebied rond het grensvlak waarbij de richting van de elektronspin kan omklappen.

**Tunneljuncties**

Deel II van dit proefschrift gaat over de spin-polarisatie van de stroom in N/barrière/S-tunneljuncties. Deze polarisatie is gemeten met de methode die bekend staat als spin-polarized tunneling. De junctions zijn met sputterdepositie en plasma-oxidatie bij kamertemperatuur gefabriceerd.

Hoeftgust 10 bespreekt resultaten verkregen met aluminium en vanadium supergeleidende elektroden die bovenop de barrière zijn gedeponeerd. In deze configuratie is het verkrijgen van voldoende junctionskwaliteit relatief moeilijk gebleken. In geval van een supergeleidende aluminium onder-elektrode daarentegen, is ontdekt dat herhaaldelijk een toereikend hoge junctionskwaliteit, overgangstemperatuur en kritisch veld verkregen kan worden door voorafgaand aan het aluminium een zeer dunne magnesium laag te deponeren.

Hoeftgust 11 behandelt een aspect van tunneljuncties wat recentelijk erkend is, namelijk de afhankelijkheid van de spin-polarisatie van het gebruikte materiaal voor de barrière. Om deze afhankelijkheid te onderzoeken zijn Al/barrière/Co(Fe)-juncties met verschillende materialen voor de barrière gebruikt. Tussen de spin-polarisatie in junctions met AlO_x en MgO als barrière is een significant verschil waargenomen. Met een AlO_x-barrière is de polarisatie ongeveer +40 % en met een MgO-barrière ongeveer +30 %. Verscheidene aanwijzingen ondersteunen dat dit verschil op intrinsieke wijze wordt bepaald door het gebruikte barrièremateriaal. De Zeeman-splitsing in de geleiding-spanning karakteristiek van junctions met HfO_x en TaO_x als barrière is niet waar te nemen. Dit wordt waarschijnlijk veroorzaakt door de zware hafnium en tantalum atomen aan het Al/barrière-grensvlak die een hoge spin-baanverstrooiing in de supergeleider induceren.

Hoeftgust 12 beschrijft een uniek onderzoek naar de rol van de diffusie van mangaanatomen in de thermische stabiliteit van de spin-polarisatie. Thermische stabiliteit is cruci-
aal voor een succesvolle integratie van tunneljuncties in de bestaande halfgeleider-industrie. Het is bekend dat boven 250 °C het magnetoweerstandseffect van magnetische tunneljuncties degradeert. Het wordt in het algemeen aangenomen dat de diffusie van mangaan hiervoor verantwoordelijk is.

De spin-polarisatie ligt ten grondslag aan het magnetoweerstandseffect. De thermische stabilitéit van deze parameter is met de spin-polarized tunneling methode direct bestudeerd. Hiervoor zijn Al/AlOₓ/Co- en Al/AlOₓ/Co₉₀Fe₁₀-juncties gebruikt zowel met als zonder een extra laag FeMn gedeponeerd bovenop de ferromagnetische elektrode. De mangaan-diffusie van de laag FeMn naar de AlOₓ-barrière is onafhankelijk bevestigd met X-ray photoelectron spectroscopy. Het is vastgesteld dat alle juncties samen met hun spin-polarisatie tot aan 500 °C thermisch stabiel zijn. Dit toont aan dat de diffusie van mangaan geen waarneembare invloed heeft. De polarisatie blijft echter alleen behouden als de juncties worden verwarmd in een voldoende schone omgeving. Bij minder schone omstandigheden degradeert de polarisatie boven 250 °C op eenzelfde wijze als waargenomen voor het tunnelmagnetoweerstandseffect. De degradatie van de polarisatie is mogelijk veroorzaakt door onzuiverheden die vanuit de omgeving in de junctie diffunderen.
List of publications

Origin of spin polarization decay in point contact Andreev reflection
C.H. Kant, O. Kurnosikov, A.T. Filip, P. LeClair, H.J.M. Swagten and W.J.M. de Jonge,

Interface spin-flip scattering model for point contact Andreev reflection
C.H. Kant, O. Kurnosikov, A.T. Filip, H.J.M. Swagten and W.J.M. de Jonge,

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C.H. Kant, J.T. Kohlhepp, H.J.M. Swagten and W.J.M. de Jonge,

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Mn diffusion and the thermal stability of tunneling spin polarization,
W.J.M. de Jonge,
Over de auteur

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