Ph.D. THESIS

Local probing of electronic transport with point contact Andreev reflection measurements

Attila Geresdi

Supervisor: Prof. György Mihály
Department of Physics
Budapest University of Technology and Economics

BUTE
2011
CONTENTS

3.3.3 Mechanical stability ............................................. 54
3.3.4 Pulsed measurements ............................................ 55
3.3.5 Simultaneous Andreev reflection and pulsed measurements .... 57
3.4 Computer control .................................................... 59

4 Spin polarization and coherent diffusive effects .................. 61
4.1 Sample details ....................................................... 61
4.2 Accuracy of the spin polarization measurements ................ 62
  4.2.1 Ballistic point contacts ........................................ 62
  4.2.2 Ballistic-diffusive crossover ................................... 64
4.3 Coherent diffusive effects ......................................... 65
  4.3.1 Junction size and temperature dependence ................... 65
  4.3.2 Statistical analysis of the ZBP properties .................... 67
  4.3.3 Discussion ..................................................... 69
4.4 Conclusions ......................................................... 70

5 The spin diffusion length in metals ................................. 72
5.1 Experimental details ................................................ 73
  5.1.1 Sample preparation ............................................. 73
  5.1.2 The measurement setup ....................................... 73
5.2 Measurements on the Fe/Au sample ................................ 73
5.3 The spin diffusion length in Pt .................................... 75
  5.3.1 Experimental results .......................................... 75
  5.3.2 Discussion ..................................................... 78
5.4 Conclusions of the spin diffusion measurements ............... 79

6 Resistive switching in the Ag$_2$S-Ag memristive system ........ 81
6.1 Sample preparation and characterization .......................... 81
6.2 $I-V$ curve measurements ......................................... 83
  6.2.1 Measurement setup ............................................. 83
  6.2.2 Composition dependence ....................................... 84
  6.2.3 Size dependence ............................................... 86
6.3 Pulsed bias measurements ......................................... 89
6.4 Investigation of the conductance channels ....................... 91
  6.4.1 Measurement setup ............................................. 92
  6.4.2 Experimental results .......................................... 92
  6.4.3 Discussion ..................................................... 93
6.5 Conclusions ......................................................... 95

A Calculation of the reflection probabilities in the BTK theory .... 97

Summary ................................................................. 101

List of publications .................................................... 103
Chapter 1
Introduction

The rapid evolution of the computer industry has been driven by the continuous miniaturization of the electronic circuitry for the last three decades. The ongoing development of computing hardware, data storage and processing elements relies on the progressive shrinking of their fundamental building blocks [1]. Even though pushing the limits to very small characteristic sizes requires significant efforts, the evolution of microelectronics has not resulted in fundamentally new design paradigms, the basic circuit elements involved have been the same for many decades. In contrast, the new era of nanoelectronics relies on physical processes observable only on the nanometer scale. This approach has led to many novel schemes, which can eventually replace today’s semiconductor-based computer architectures due to their favorable properties in terms of size, data storage density or power consumption.

A widely investigated field of nanoelectronics is spintronics, which relies on the coherent propagation of the electronic spin [2–4]. While the concept and description of spin polarized electronic transport dates back to the pioneering work of Mott [5], experimental investigation of such phenomenon demands creating metallic structures smaller than the characteristic length scale of the decay of spin information, the spin diffusion length, typically in the order of 10 nm to 100 nm [6]. The discovery of the giant magnetoresistance (GMR) in ferromagnetic – nonmagnetic – ferromagnetic (FM/NM/FM) layered structures [7,8] demonstrated the persistence of a nonequilibrium spin population in the nonmagnetic layer over the spin diffusion length [9]. Devices, like spin valves, were fabricated based on novel material systems, such as carbon-based nanostructures as well [10,11], and further developments made nonlocal measurements possible [12,13].

Another intriguing concept is the utilization of the permanent influence of charge current on certain materials. The study of memristors (memory resistors) started with the theoretical proposal of L. Chua in 1971 [14], however unambiguous experimental demonstration lacked until 2008 [15]. Due to its favorable properties, such as high speed operation, long data retention and high integrability, resistive random access memory (RRAM) based on memristive materials is a widely investigated concept [16, 17] to replace today’s solid state memories. Specifically, it has been demonstrated, that digital data can be stored with the formation and retraction of metallic filaments in a semiconducting matrix [18], and shown to be scaled down to the single atomic
limit [19]. Even though crossbar architecture devices storing digital data have already been prepared [20,21], and fabrication schemes using no supplementary semiconductor elements have been published [22], the field is still interesting for fundamental research as well, since the details of the resistive transitions are in general not well understood [23,24].

The evolution of nanoelectronics demands novel means of investigation of physical properties in contrast to bulk transport or spectroscopy methods. Moreover, further advances down to the ultimate limit of single atomic devices cannot be made by simply scaling down present day’s sample fabrication techniques. It is therefore essential to develop local probing methods which can reliably characterize or even manipulate nanoscale devices.

This Ph.D. thesis summarizes my systematic study of point contacts with typical sizes below 100 nm, down to the single atomic regime. In this experimental work, I utilize superconductivity as a local probe, capable of sensing the transmission of a nanoscale junction, or even extracting information on the electronic spin polarization of the studied material. This opens up many possibilities to investigate the different physical processes on the nanometer scale, such as the transition of the resistance in memristive systems, or the decay of the spin polarization in the nonmagnetic layer of spin valve systems.

All these possibilities are based on the special charge conversion process, first described by A. F. Andreev in 1964 [25]. This process, called the Andreev reflection, is the simultaneous transmission of two charge quanta, which can be expressed as a reflected hole-like quasiparticle in place of the incoming electron. The Andreev reflection is the only source of charge transfer for subgap bias voltages, where no direct quasiparticle transfer can occur. It was shown by the work of Blonder, Tinkham and Klapwijk in 1982 [26,27], that in a good quality SN junction, the subgap conductance can be twice as large as the conductance at high bias. This is related to the transfer of two elementary charges as opposed to the single particle transfer far above the superconducting gap [28,29].

Andreev reflection measurements were initially performed in order to investigate exotic superconductors, such as compounds exhibiting d-wave ordering [30], or even multiple gap features [31]. In these experiments, the superconductor was probed using a simple metallic electrode, and investigated for the details of the superconducting ordering. Later, the structure of the atomic orbitals of superconducting metals has been analyzed by employing the scheme of multiple Andreev reflections [32,33].

Andreev reflection has also become an important tool of nanophysics because of the spin constraint between the incoming electron and the reflected hole. That is, in order to have a spin singlet Cooper pair condense at the superconductor side, the reflected hole has to possess opposite spin orientation as the incoming electron. Based on this property, the degree of spin ordering can be deduced in the normal metallic side of the junction, as it was demonstrated by Soulen et al. in 1998 [34] and has been frequently used since then [35–38].

During my Ph. D. work at Department of Physics of the Budapest University of
Technology and Economics, my research was focused on the utilization of Andreev reflection for the detection of local spin polarization and the investigation of the memristive materials, both having a great fundamental importance in novel computer applications, such as data processing and memory devices.

The outline of this thesis is as follows: First, in Chapter 2, an introduction of the field of nanoscale point contacts is given, concentrating on superconducting – normal heterojunctions and covering both earlier experimental and theoretical works. Previous results on the spin valve devices and memristive materials are also briefly summarized.

The experimental techniques applied in my PhD work are discussed in Chapter 3. Since the construction of the measurement setup was an essential part of my work, the design considerations and characterization are discussed in detail.

In Chapter 4, I describe the Andreev reflection measurements in terms of reliability. By evaluating measurement data on the magnetic (In,Mn)Sb and nonmagnetic (In,Be)Sb compound, the importance of employing point contacts in the ballistic limit is demonstrated. For large junctions, however, additional phenomena attributed to coherent diffusive backscattering are found.

My measurements concerning the spin diffusion length in nonmagnetic metals are shown in Chapter 5. The role of different sources of spin relaxation are demonstrated. The observed spin diffusion length is compared to earlier experimental data for the same geometry, and a good agreement is found.

In Chapter 6, the characterization of the Ag-Ag$_2$S based memristive system is given. By tuning the sample preparation parameters, I observed various electronic behaviors, including metallic conductance down to cryogenic temperatures. Moreover, very short pulse times ($\sim 10$ ns) were enough to alter the resistance of the device. I have also applied Andreev reflection measurements to investigate the electrochemical process responsible for the resistive switching phenomenon.

Finally, I summarize my work in five thesis points.
Chapter 2

Overview of the research field

2.1 Electron transport in nanocontacts

Nanocircuits, in which two (or more) macroscopic conductors are connected through a nanoscale constriction show several interesting phenomena. The simplest nanoconstriction is a small point contact connecting two electrodes. Such point contacts act as local probes, their behavior significantly influenced by the scattering processes in the narrow neighborhood of the contact. Accordingly, the theoretical description of such nanocontacts is based on the decomposition of the physical system to perfect leads and the point contact in between. The scattering processes are then limited to the contact region, whereas the leads act as reservoirs determining the distribution function of the charge carriers. This decomposition makes the theoretical description of the nanojunction more convenient, as the contact region is usually smaller, thus easier to handle, and one does not have to take the details of the leads into account. Following this scheme, the basic description of the electronic transport in point contacts is given in this section.

2.1.1 Length scales

The conductance of a macroscopic conductor is described by Ohm’s law:

\[ G = \sigma \frac{A}{l}, \]  

where \( A \) and \( l \) are the cross-section and length of the conductor, respectively. The \( \sigma \) conductivity of the sample is determined by intrinsic material parameters, first described by the Drude conductivity:

\[ \sigma = \frac{n e^2}{m} \tau_m, \]  

where apart from the charge carrier concentration \( n \), the only free parameter is \( \tau_m \), the characteristic momentum relaxation time of the charge carriers. This simple picture is, however, not valid for arbitrary small conductors, and inherently fails if the size of the structure becomes so small, that the electron crosses it in a timescale of \( \tau_m \).
2.1. ELECTRON TRANSPORT IN NANOCONTACTS

The associated length scale is \( l_m = v_F \tau_m \), with \( v_F \) being the Fermi velocity of the electron. This quantity determines the distance, that the electron traverses between two scattering events. A nanoconstriction is in the **ballistic regime** if \( l \ll l_m \), i.e. essentially no scattering occurs inside the conductor (Fig. 2.1a). On the contrary, for conductors in the **diffusive regime** many scatterings occur, so that \( l \gg l_m \) (Fig. 2.1b). Mesoscopic systems with \( l \sim l_m \) are defined to be in the **intermediate regime**. The description of the electronic transport in each regime will be discussed in detail later.

Other scattering processes define additional length scales in a nanoscale system (Fig. 2.2). Specifically, inelastic processes occur on the length scale of \( l_\phi \), the phase-coherence length, over which the electrons preserve their quantum coherence, hence quantum interference phenomena, such as Aharonov-Bohm oscillations, conductance fluctuations and weak localization occur only in structures smaller than \( l_\phi \) [39]. The decay of coherence of a charge carrier is caused by electron-phonon and electron-electron...
scattering, as well as scattering on magnetic impurities, whereas pure elastic scattering does not affect quantum coherence. Hence, both ballistic and diffusive conductors can be phase coherent over a certain \( l_\phi \) length scale. For a ballistic system \( l_\phi = v_F \tau_\phi \) holds, while in diffusive conductors \( l_\phi = \sqrt{D \tau_\phi} \) with \( D \) being the diffusion coefficient.

Similarly to the persistence of the phase information of the orbital wave function, another length is defined, over which the spin information is conserved. The spin-flip length \( l_s \) has fundamental role in spintronic applications, thus it is widely studied both theoretically and experimentally.

Usually it is assumed that a mesoscopic conductor can be described with semiclassical arguments. However for systems with typical feature size comparable to the Fermi wavelength \( (\lambda_F) \) this is not the case, and full quantum description is necessary. This regime, where the quantized behavior of the electronic transport is of importance, will be addressed later. First, the quasiclassical theory of electronic transport is presented, which is valid for systems much larger than \( \lambda_F \).

### 2.1.2 Diffusive and ballistic regime

The conductance of a point contact in the diffusive regime can be addressed classically by solving the Maxwell equations. In the DC limit, the electric potential fulfills the Poisson equation:

\[
\Delta \Phi(\vec{r}) = 0. \tag{2.3}
\]

Additionally, Ohm’s law is taken into account, connecting the local density of current and the electric field:

\[
\vec{j}(\vec{r}) = \sigma \vec{E}(\vec{r}). \tag{2.4}
\]

The conductance in this limit was first evaluated by J. C. Maxwell [40] for the case of the orifice-like constriction, i.e. a circular hole connecting two bulk regions:

\[
G = 2\sigma a, \tag{2.5}
\]

where \( a \) is the radius of the orifice and \( \sigma \) is the conductivity of the material.

In the ballistic regime, the electrons do not scatter in the contact region, therefore their energy distribution is preserved: all the left-mover electrons with \( k_x < 0 \) possess the distribution of the right electrode, i.e. these states are filled up to the chemical potential of the right electrode, \( \mu_R \). On the other hand, the right moving states with \( k_x > 0 \) are occupied up to \( \mu_L \), the chemical potential of the left electrode (Fig. 2.3).

The current density can be written as:

\[
\vec{j} = \frac{2e}{V} \sum_k \vec{v}(\vec{k}) f_k, \tag{2.6}
\]

with \( V \) being the volume of the system. Here, the net current is provided by the uncancelled portion of the right-movers in a

\[
dk = \frac{d\varepsilon}{\hbar v_F} = \frac{eV}{\hbar v_F} \tag{2.7}
\]
Figure 2.3: (a) Inside the junction, all electrons moving to the left possess the distribution of the right electrode, whereas electrons coming from the left electrode preserve the distribution characteristic to the left electrode. The distributions in the two electrodes are also plotted far away from the junction. (b) Occupied electronic states in the two electrodes. The states between $\mu_L$ and $\mu_R$ are responsible for the net current induced by the applied bias voltage, $V$.

thick belt around $k_F$ in the reciprocal space. Substituting into (2.6), we get the Sharvin formula [41] for a three dimensional system after straightforward calculations:

$$G_S = \frac{2e^2}{h} \left( \frac{k_F a}{2} \right)^2,$$

(2.8)

with $a$ being the radius of the junction. It is to be noted, that in contrast to (2.5) no scattering processes is included inside the junction area. This is a natural consequence of the ballistic assumption. However inelastic scatterings in the leads are essential to thermalize the electrons in each lead. This is the reason why all the incoming electrons can be described by the distribution function of their source lead.

For junction diameters that are comparable to the mean free path, no analytical solution exists. However approximate formulae can be given by numerically solving the Boltzmann equation for the specific geometry. A frequently used approximation is the Wexler equation [42,43]:

$$R_W = \frac{4l_m}{3\sigma r^2 \pi} + \gamma \left( \frac{l_m}{d} \right) \frac{1}{2r\sigma},$$

(2.9)

where $\gamma$ is a monotonous function ranging from $\gamma(0) = 1$ to $\gamma(\infty) \approx 0.69$. A notable property of (2.9) is that it can be decomposed as the sum of the resistances obtained
in the ballistic and in the diffusive regime. Considering the Drude conductivity (2.2) with \( l_m = v_F \tau \), it is apparent that \( l_m / \sigma \) is constant in the first term, and the reciprocal of the Sharvin conductance (2.8) is recovered. The importance of (2.9) is that it provides a good estimation of the junction size if the junction resistance and the material parameters are known.

### 2.1.3 Landauer formalism

![Figure 2.4: (a) The first four eigenmodes in a constriction described by (2.10). (b) For the propagating modes, the \( \varepsilon_n(k) \) dispersion crosses the Fermi energy. (c) The net current for each mode is carried by an \( eV \) energy window. Occupied states are denoted by the thick line plot.](image)

In order to address the electrical transport of nanoconstrictions with feature sizes comparable to the Fermi wavelength (\( \lambda_F \)), the calculations based on semiclassical arguments cannot be used, and one has to consider each propagating wavefunction inside the wire [44]. Below we discuss a simple two dimensional case with a hard wall potential. The Hamiltonian is written as:

\[
\mathcal{H} = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + V(y)
\]

with

\[
V(y) = \begin{cases} 
0 & \text{if } 0 < y < d \\
\infty & \text{otherwise}. 
\end{cases}
\]

In this case, the eigenfunctions are the following (Fig. 2.4a):

\[
\Psi_n(x, y) = e^{ikx} \sin \left( \frac{n\pi y}{d} \right)
\]

with the corresponding energy dispersion:

\[
\varepsilon_n(k) = \frac{\hbar^2 k_x^2}{2m} + \frac{\pi^2 \hbar^2}{2md} n^2
\]
The notation \( k \equiv k_x \) emphasises that the propagation is possible solely along the \( x \) direction. Only a finite number of channels fulfill the condition \( \varepsilon_n(0) < \varepsilon_F \) and contribute to the conductance (Fig. 2.4b). First, we calculate the conductance of an ideal wire with no backscattering using similar arguments that led to (2.8). A finite voltage drop through the junction is considered as the shift of the chemical potentials in the two leads as demonstrated in Fig. 2.4c. The net current can be written as follows:

\[
I = I_{L \to R} - I_{R \to L} = \frac{2e}{L} \sum_{k,n} v(k)(f_L(k) - f_R(k)) = \frac{2e}{\hbar} M \int (f_L(\varepsilon) - f_R(\varepsilon)) d\varepsilon, \quad (2.14)
\]

with \( M \) being the number of the open channels. By evaluating the integral and substituting \( \mu_L - \mu_R = eV \), the conductance is:

\[
G = \frac{2e^2}{\hbar} M = G_0 M. \quad (2.15)
\]

\[
|in\rangle_L \quad \rightarrow \quad S \quad \rightarrow \quad |in\rangle_R
\]

\[
|out\rangle_L \quad \leftarrow \qquad |out\rangle_R
\]

Figure 2.5: The scattering processes inside the constriction are represented by the scattering matrix \( S \) connecting the \( |in\rangle \) and \( |out\rangle \) vectors (2.16).

Now we consider the more realistic description of the constriction, where scatterings between the channels are present (Fig. 2.5.). This is described by the scattering matrix [45], connecting the incoming and outgoing wavefunctions at the scatterer. It is defined as:

\[
|out\rangle = S|in\rangle \quad (2.16)
\]

The scattering matrix can then be rewritten in the following block representation for two terminals:

\[
S = \begin{bmatrix} r & t' \\ t & r' \end{bmatrix} \quad (2.17)
\]

with the decomposition of the \( |in\rangle \) and \( |out\rangle \) vectors:

\[
|in\rangle = \begin{bmatrix} |in\rangle_L \\ |in\rangle_R \end{bmatrix} \quad \text{and} \quad |out\rangle = \begin{bmatrix} |out\rangle_L \\ |out\rangle_R \end{bmatrix} \quad (2.18)
\]

Thus the transmission matrix \( t \) couples the incoming mode on the left side to the outgoing mode on the right side:

\[
|out\rangle_R = t|in\rangle_L. \quad (2.19)
\]
It can be shown that the conductance is simply calculated from the transmission matrix as [45, 46]:

\[
G = \frac{2e^2}{h} \text{Tr}(t^\dagger t) = \frac{2e^2}{h} \sum_{i=1}^{M} T_i
\]  

(2.20)

where the \( T_i \) values are the eigenvalues of the \( t^\dagger t \) matrix, each in the \([0...1]\) range. This follows from \( SS^\dagger = 1 \), i.e. \( S \) is unitary due to the charge current conservation through the contact. This property of the \( T_i \) values provides a statistical description of the scattering over an ensemble of electrons: one can identify \( T_i \) as the probability that an incoming electron in the eigenmode \( i \) gets transmitted. Hence, other transport properties, such as current noise [47, 48] and fluctuations [49] can be described on the basis of the \( T_i \) values as well.

Note the appearance of the universal \( G_0 = 2e^2/h \approx (12.9\text{k}\Omega)^{-1} \) conductance value, the conductance quantum. This recalls that the quantum nature of the conductance should be considered if there are only a few propagating channels, i.e. \( M \) is small and \( R \sim G_0^{-1} \) [50].

## 2.2 Spin polarized transport

### 2.2.1 Landauer formalism in ferromagnets

Previously it was assumed that the eigenmodes of the Hamiltonian (2.10) are spin-degenerate. This is indeed the case for nonmagnetic systems, however, in ferromagnets an additional exchange term \(-\sigma\varepsilon_\text{ex}\) has to be added with \( \sigma = \pm 1/2 \) resulting in a splitting of the two spin subbands. Consequently, both the transmission eigenvalues and the number of the open channels can differ for the spin up and spin down subbands as illustrated in Fig. 2.6.

![Figure 2.6](image)

**Figure 2.6:** (a) The representation of the first two eigenmodes in a ferromagnetic wire. (b) The corresponding dispersion for the majority (blue) and for the minority (red) spin channels, respectively.

Assuming that spin-flip scatterings are negligible, the net conductance is the sum
of the conductances of the two spin channels:

\[ G = \sum_{\sigma} G_{\sigma} = G_{\uparrow} + G_{\downarrow} = \frac{e^2}{h} \sum_{i=1}^{M_{\uparrow}} T_{i\uparrow} + \frac{e^2}{h} \sum_{i=1}^{M_{\downarrow}} T_{i\downarrow}. \]  

(2.21)

Note, that the prefactor \( \frac{e^2}{h} \) is the half of the previous value due to the absence of spin degeneracy. Without any further assumptions, (2.21) can be rewritten as:

\[ G = \frac{e^2}{h} \left( M_{\uparrow} \bar{T}_{\uparrow} + M_{\downarrow} \bar{T}_{\downarrow} \right). \]  

(2.22)

Here, \( M_{\uparrow} \) and \( M_{\downarrow} \) are the number of propagating channels in the majority and minority spin bands, respectively. \( \bar{T}_{\uparrow} \) and \( \bar{T}_{\downarrow} \) denote the average transmission probabilities. In a typical mesoscopic conductor, the level spacing is small compared to \( \varepsilon_{ex} \) and \( \varepsilon_F \), thus many open channels exist (Fig. 2.7). In this case, the source of the spin polarization of the current can be both \( M_{\uparrow} \neq M_{\downarrow} \) and \( \bar{T}_{\uparrow} \neq \bar{T}_{\downarrow} \).

![Figure 2.7: The dispersion in a ferromagnetic mesoscopic system exhibiting exchange splitting. The number of the open channels is denoted by \( M_{\uparrow} \) and \( M_{\downarrow} \) for the majority and minority spin subband, respectively.](image)

The spin polarization of the current is defined as:

\[ P_c = \frac{I_{\uparrow} - I_{\downarrow}}{I_{\uparrow} + I_{\downarrow}} = \frac{\sum_{i=1}^{M_{\uparrow}} I_{i\uparrow} - \sum_{i=1}^{M_{\downarrow}} I_{i\downarrow}}{\sum_{i=1}^{M_{\uparrow}} I_{i\uparrow} + \sum_{i=1}^{M_{\downarrow}} I_{i\downarrow}} = \frac{M_{\uparrow} \bar{T}_{\uparrow} - M_{\downarrow} \bar{T}_{\downarrow}}{M_{\uparrow} \bar{T}_{\uparrow} + M_{\downarrow} \bar{T}_{\downarrow}}. \]  

(2.23)

assuming linear conductance so that \( I_{\sigma} = G_{\sigma} V \). Considering (2.6), one can relate the current density of each mode to the band parameters of the corresponding channel:

\[ I_{\sigma} \propto T_{\sigma} \rho_{\sigma}(\varepsilon_F) v_{\sigma}(\varepsilon_F). \]  

(2.24)

Upon summing up for the open channels, we get:

\[ I_{\sigma} \propto \bar{T}_{\sigma} \sum_{i=1}^{M_{\sigma}} \rho_{\sigma}(\varepsilon_F) v_{\sigma}(\varepsilon_F). \]  

(2.25)
2.2. SPIN POLARIZED TRANSPORT

Even though the individual \( T_i \) values depend on the details of the scatterings in the nanojunction, for \( M_\sigma \gg 1 \), the ensemble average for the two spin subbands is assumed to be the same. In this mesoscopic limit, \( (2.23) \) can be further simplified, because the \( T_\sigma \) values drop out:

\[
P_c = \sum_{i=1}^{M_{\uparrow}} \rho_i(\varepsilon_F) v_i(\varepsilon_F) - \sum_{i=1}^{M_{\downarrow}} \rho_i(\varepsilon_F) v_i(\varepsilon_F),
\]

\( (2.26) \)

When considering the Fermi surface properties for many propagating channels, the \( v_{\sigma i}(\varepsilon_F) \) distinct Fermi velocity values can be replaced with an average \( \bar{v}_{\sigma}(\varepsilon_F) \) over the propagating modes, and the the density of states can be summed up:

\[
P_c = \frac{\rho_\uparrow(\varepsilon_F) \bar{v}_\uparrow(\varepsilon_F) - \rho_\downarrow(\varepsilon_F) \bar{v}_\downarrow(\varepsilon_F)}{\rho_\uparrow(\varepsilon_F) \bar{v}_\uparrow(\varepsilon_F) + \rho_\downarrow(\varepsilon_F) \bar{v}_\downarrow(\varepsilon_F)}
\]

\( (2.27) \)

This expression of the current polarization is often used in conjunction with spin polarization measurements in ballistic point contacts. As we will see in Section 2.4.2, the recovered spin polarization evaluates to \( (2.23) \) for Andreev reflection measurements, hence \( (2.27) \) can connect experimental data to ferromagnetic band structure calculations.

2.2.2 Band structure of ferromagnets

First, we present the basic features of spin-splitted bands in metallic ferromagnets. Next, we describe the band structure of the dilute magnetic semiconductors, which was used as a model system for our Andreev reflection measurements.

Itinerant ferromagnets

A simplified \( \rho(\varepsilon) \) density of states of ferromagnetic metals is shown in Fig. 2.8. In ferromagnetic transition metals, typically the d or f bands are shifted due to the exchange splitting. The magnetization is then defined by the following equation:

\[
M = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow}
\]

\( (2.28) \)

with \( N_\sigma = \int \rho_\sigma(\varepsilon) f(\varepsilon) d\varepsilon \). The magnetization is accessible to bulk magnetization measurement methods, such as SQUID or VSM. In contrast, in experiments concerning electronic transport, the Fermi surface properties are relevant. Based on the band structure one can define the spin polarization of the density of states at the Fermi energy:

\[
P = \frac{\rho_\uparrow(\varepsilon_F) - \rho_\downarrow(\varepsilon_F)}{\rho_\uparrow(\varepsilon_F) + \rho_\downarrow(\varepsilon_F)}
\]

\( (2.29) \)

The fundamental difference between \( P \) and \( M \) is well demonstrated by the simplified band structure of Co and Ni in Fig. 2.8a. Here, the Fermi energy crosses the d band.
for the minority spins, whereas for the majority spins the d band is below the Fermi energy. In this case $M > 0$ and $P < 0$ holds, i.e. the spin polarization at the Fermi level has opposite sign to the magnetization. In contrast, for other materials, such as Fe, $M > 0$ and $P > 0$ as sketched in Fig. 2.8b.

The Fermi surface spin polarization $P$ can be probed via spectroscopy methods such as the spin and angle resolved photoelectron spectroscopy (SARPES) [51]. Other experimental methods generally extract different values, e.g. Andreev reflection typically probes $P_c$ defined in (2.27), as we will see in Section 2.4.2. This quantity, in general differs both from $P$ and $M$, therefore care must be taken when comparing experimental data obtained by different experimental methods.

**Dilute magnetic semiconductors**

Dilute magnetic semiconductor (DMS) compounds have recently gained interest as a possible link from from semiconductor based electronics to spintronic applications [52, 53]. It was shown that most of the III-V semiconductors exhibit ferromagnetic ordering if Mn dopants are introduced in a typical concentration of 2 – 10 at% [54] opening the possibility of the integration of ferromagnetic materials into a semiconductor electronic circuit. Moreover, the electronic control of the magnetic properties has also been demonstrated in such compounds [55–57]. Despite the apparent limit of the Curie temperatures below room temperature [58] and the complicated sample preparation procedure providing Mn concentrations well above the equilibrium solubility limit [59], these compounds are of fundamental interest because of the unique interplay between magnetism and electronic transport [60, 61].

The ferromagnetic ordering in the (III,Mn)V compounds is well described by a carrier mediated superexchange model: The localized Mn$^{2+}$ ions with $S = 5/2$ magnetic moment are antiferromagnetically coupled to the itinerant holes in the p band [62].
2.2. SPIN POLARIZED TRANSPORT

Figure 2.9: The density of states of the Zener model consisting of very narrow d bands, and itinerant holes. Due to the antiferromagnetic coupling, the sign of the splitting is opposite for the two bands.

Consequently, an effective coupling emerges between the localized moments which is described by the Heisenberg Hamiltonian:

\[ H = - \sum_{i,j} J(r_{ij}) \vec{S}_i \cdot \vec{S}_j \]  \hspace{1cm} (2.30)

The spatial variation of the \( J(r_{ij}) \) effective magnetic coupling in an arbitrary dilute magnetic alloy was first calculated by Rudermann, Kittel, Kasuya and Yosida (RKKY) [63] showing that it exhibits oscillations with a periodicity of \((2k_F)^{-1}\):

\[ J(r) \propto \frac{1}{(2k_F r)^4} \left( (2k_F r) \cos(2k_F r) - \sin(2k_F r) \right). \]  \hspace{1cm} (2.31)

It is important to note that this effective coupling leads to a competition of ferromagnetic and antiferromagnetic ordering for magnetic impurities in a paramagnetic metallic matrix where the typical \( k_F r \gg 1 \). This leads to the spin glass behavior which is not addressed in this work. For DMS systems, however, the localized Mn\(^{2+}\) ions are the source of the charge carriers as well, hence \( k_F r \sim 1 \) holds resulting in an effective ferromagnetic coupling. Moreover, the coupling between the localized d moments and the conducting p holes can be regarded as an on-site interaction, whereas the effective coupling (2.31) is long range, since \( k_F \) is small. This limit is described by a simplified model developed by Zener [64,65]. The corresponding band structure is shown in Fig. 2.9.

2.2.3 Spin relaxation

In metals, the dominating spin-flip process is the Elliott-Yafet relaxation [66,67]. This mechanism is originated from the coupling between the spin and orbital degree of freedom described by the spin-orbit coupling Hamiltonian:

\[ H_{SO} = \frac{\hbar^2}{4m^2c^2} \vec{\sigma} \left( \vec{\nabla} V \times \vec{k} \right). \]  \hspace{1cm} (2.32)
Including this term in the Hamiltonian of the charge carriers, the resulting eigenfunctions are a mixture of spin up and spin down states:

\[ \Psi_{\uparrow n\vec{k}} = (a_{n\vec{k}}| \uparrow \rangle + b_{n\vec{k}}| \downarrow \rangle)u_{n\vec{k}}(\vec{r})e^{i\vec{k}\cdot \vec{r}}, \tag{2.33} \]

\[ \Psi_{\downarrow n\vec{k}} = (a_{n\vec{k}}^*| \downarrow \rangle + b_{n\vec{k}}^*| \uparrow \rangle)u_{n\vec{k}}(\vec{r})e^{i\vec{k}\cdot \vec{r}} \tag{2.34} \]

where \( u_{n\vec{k}}(\vec{r}) \) is the oscillatory part of the Bloch function determined by the atomic potentials. The spin index of each \( \Psi \) wavefunction is still used assuming that \( H_{SO} \) is a small perturbation, hence \( |a_{n\vec{k}}| \gg |b_{n\vec{k}}| \). In first order of perturbation, \( b_{n\vec{k}} \) can be evaluated using the corresponding matrix element of the spin-orbit coupling, and the energy difference between the given \( \vec{k} \) state in the \( n' \) and \( n \) bands:

\[ b_{n\vec{k}} = \sum_{n'} \frac{\langle H_{SO} \rangle_{nn'}(\vec{k})}{E_{n'}(\vec{k}) - E_n(\vec{k})} \tag{2.35} \]

As the denominator is in the 1 eV range and the spin-orbit coupling is typically much smaller, indeed \( b_{n\vec{k}} \ll 1 \) follows.

Figure 2.10: The scheme of the Elliott-Yafet mechanism of spin relaxation.

The spin relaxation is then attributed to scattering processes of the electrons changing the \( \vec{k} \) state, hence altering the weight of each spin subbands (Fig. 2.10). Thus, \( t_s \) can be estimated as \[67\]:

\[ t_s^{-1} \approx \langle \tilde{b}^2 \rangle \tau_m^{-1} \tag{2.36} \]

where \( \tau_m \) is the momentum relaxation time. It should be noted, however, that the exact scaling factor depends on the source of the actual scattering process, e.g. electron-phonon interaction, boundary or impurity scattering. In bulk metals, the electron-phonon interaction governs \( \tau_m \) over a wide temperature range, thus \( t_s \) follows the Bloch-Grüneisen law similarly to the resistivity of the material \( t_s^{-1} \sim \rho(T) \) \[68\].

It is important to note that in the above discussion the spin relaxation time \( t_s \), i.e. the characteristic time scale for the persistence of the spin information was considered. In many cases, however, the associated length scale \( l_s \) can be measured directly.
In order to find the correspondence, we have to distinguish between ballistic and diffusive spin transport. In the ballistic regime \( t_s \sim \tau_m \), \( l_s = v_F t_s \) with \( v_F \) the Fermi velocity, whereas for diffusive propagation \( t_s \ll \tau_m \) \( l_s = \sqrt{D t_s} \) follows, with \( D \) being the diffusion coefficient. Typically, within the framework of Elliott and Yafet, equation (2.36) demands the second case, as \( \langle b^2 \rangle \ll 1 \). This condition is often confirmed by experimental data as well \[4, 69, 70\].

It should be noted that other mechanisms may also contribute to the spin relaxation and have to be taken into account depending on the physical system investigated. The D’Yakonov-Perel’ mechanism \[71, 72\] occurs in noncentrosymmetric semiconductors typically described by the Rashba or the Dresselhaus Hamiltonian. Here, \( \varepsilon_\uparrow(\vec{k}) \neq \varepsilon_\downarrow(\vec{k}) \) results in an effective \( \vec{B}(\vec{k}) \) magnetic field causing a precession of the spin. Another channel for spin relaxation is the exchange interaction with localized spins. Notable examples are the Bir-Aronov-Pikus relaxation \[73\] in p-doped semiconductors and the hyperfine interaction coupling the spin of the electrons and the nuclei \[74\].

### 2.3 Superconductor–normal metal junctions

In the previous sections, we calculated the conductance of point contacts between two metallic conductor leads. In this section, we will consider the influence of a superconductor ordering in one of the leads resulting in nonlinear differential conductance. First, following the work of Blonder, Tinkham and Klapwijk (BTK, \[26\]), we calculate the transport properties of a ballistic superconductor–normal metal (SN) junction based on the scattering matrix approach. Afterwards we comment on the influence of diffusive transport on the results.

#### 2.3.1 BTK theory

A simple model of a SN junction can be discussed within the framework of the BTK theory \[26\]. Here, we consider a one dimensional ballistic channel with a step-like variation of the superconducting order parameter: \( \Delta(x) = \Delta \Theta(x) \). In order to include surface barrier backscattering, a Dirac delta potential centered to the interface is also included in the model:

\[
U(x) = Z \hbar v_F \delta(x).
\]  

Here, \( Z \) denotes the dimensionless barrier strength ranging from 0 to \( \infty \) as the junction transparency scales from 1 (metallic limit) to 0 (tunneling limit). The possible reflection mechanisms on the SN interface are the normal reflection (Fig. 2.11a) and the Andreev reflection (Fig. 2.11b). The former results in no charge transmission through the interface, whereas the Andreev reflection process transmits two charge quanta, which is usually described as a reflection of a hole. As the superconducting condensate consists of spin singlet Cooper pairs, the reflected hole has the opposite spin as the incoming electron.
2.3. SUPERCONDUCTOR–NORMAL METAL JUNCTIONS

Figure 2.11: Possible reflection processes on a superconductor–normal metal interface within the BTK framework: Specular quasiparticle reflection (a), and Andreev reflection (b), where the incoming electron is reflected as a hole in the opposite spin subband.

The detailed calculation of the reflection amplitudes $a(E,Z)$ and $b(E,Z)$ is given in the Appendix. Here we only give the expression of the electronic current (Fig. 2.12a and 2.12c) and the differential conductance (Fig. 2.12b and 2.12d) at finite temperatures:

$$I(V,Z) = \frac{2eN}{h} \int_{-\infty}^{\infty} dE \left( f_0(E-eV) - f_0(E) \right) (1 + A(E,Z) - B(E,Z)) \quad (2.38)$$

$$G(V,Z) = \frac{dI(V,Z)}{dV} = \frac{2e^2N}{h} \int_{-\infty}^{\infty} dE \left( -\frac{\partial f_0(E-eV)}{\partial E} \right) (1 + A(E,Z) - B(E,Z)) \quad (2.39)$$

using the notation $A(E,Z) = |a(E,Z)|^2$ and $B(E,Z) = |b(E,Z)|^2$.

Note, that the parameter $Z$ can be directly mapped to the junction transparency $T$ in the Landauer formalism. The normal state conductance for $eV \gg \Delta$ of a single channel is:

$$G_N = \frac{2e^2}{h} \frac{1}{1+Z^2} = \frac{2e^2}{h} T, \quad (2.40)$$

whereas the zero bias conductance at zero temperature reads:

$$G_{SN} = \frac{4e^2}{h} \frac{1}{(1+2Z^2)^2} = \frac{4e^2}{h} \frac{T^2}{(2-T)^2}. \quad (2.41)$$

For perfectly transparent junctions the subgap conductance is doubled, i. e. for $eV < \Delta$ and $T = 1$, i. e. the probability of Andreev reflection is 100% ($A = 1$). Thus, $G_{SN} = 2G_N$ is a direct fingerprint of the doubled charge transmission for each incoming electrons. However, for tunnel junctions ($T \ll 1$) $G_{SN} \propto T^2$ directly reveals that Andreev reflection is a second order process. In the tunneling limit, for $T \to 0$, $G_{SN}/G_N \to 0$ is expected.
2.3. SUPERCONDUCTOR–NORMAL METAL JUNCTIONS

Figure 2.12: The results of the BTK calculation. (a) and (b) The $I - V$ and $G - V$ curves of the SN junction for different values of $Z$ at zero temperature. (c) and (d) The same data at a finite temperature of $k_B T/\Delta = 0.25$ approximately corresponding to the gap of Nb at $T = 4.2K$.

2.3.2 Corrections for the diffusive regime

The scheme of Andreev reflection consists of an incoming electron from the normal metal side being transferred to the superconductor, and leaving behind a hole on the time-reversed path of the incident electron. In a ballistic case (Fig. 2.13a), this particle immediately returns to the reservoir, in contrast to the diffusive case (Fig. 2.13b), where it scatters many times near the junction area going through exactly the path of the incoming electron.

This coherent backscattering of the time-reversed particle effectively introduces superconducting pair correlations into the normal electrode, and provides a mesoscopic scheme of proximity superconductivity [75].

The influence of coherent backscattering on the conductance in mesoscopic systems
was first explored in disordered metallic nanowires [76,77], and became a versatile tool to deduce the characteristic time scales of different scattering processes [78]. Later, it was found that coherent diffusive backscattering can considerably modify the conductance of SN junctions as well [79]. In order to address this effect, we consider a diffusive volume with a characteristic length of $L$ on the N side of the junction (Fig. 2.14a) with a mean free path of $l_m \ll L$ [80]. The area of the junction is implicitly included through the number of the propagating channels, $M$. It is assumed that the diffusive volume is metallic, so that

$$L \ll M l_m$$

in contrast to the localization regime $L \gg M l_m$, (which exhibits an exponential cutoff of the conductance with increasing $L$).

In the metallic regime, the ensemble average of the transmission eigenvalues is [80,81]:

$$\langle T_N \rangle = \frac{l_m}{L}.$$  

(2.43)
Fig. 2.14b shows a simple model, where the diffusive volume is replaced by a single barrier with a transmission $T_N$ determined by (2.43). The zero bias conductance $G_{SN}$ of this system can be calculated by coherently summing the paths of the multiple scatterings. At high bias, the normal state conductance $G_N$ is acquired by incoherently summing the paths for the two barriers, each between two normal state conductors. Depending on the transparency of the SN junction, we consider two limits, as discussed below.

**Reentrant conductance**

For a perfectly transparent SN interface with $T_S = 1$, the only possible process at zero bias is the Andreev reflection, thus $a = -i$ (see the Appendix). By evaluating the zero bias conductance for a given $T_N$, we get:

$$G_{SN} = \frac{4e^2}{\hbar} \frac{T_N^2}{(2 - T_N)^2}$$

(2.44)

which is surprisingly similar to (2.41). Note however, that here the transmission eigenvalue determining the conductance is $T_N$ within the normal side of junction instead of $T_S$ on the SN boundary. The normal state conductance is:

$$G_N = \frac{2e^2}{\hbar} T_N.$$

(2.45)

By evaluating the average with random matrix theory [80], we get:

$$\langle G_{SN} \rangle = \langle G_N \rangle$$

(2.46)

instead of $\langle G_{SN} \rangle = 2\langle G_N \rangle$ expected from the ballistic theory. In experiments, the onset of the coherent backscattering is observable through the nonmonotonic temperature dependence of the zero bias conductance eventually returning to $G_N$ in the limit of zero temperature. Due to this feature it is called *reentrant conductance* [82] (Fig. 2.15).

**Reflectionless tunneling**

In the tunneling limit of the SN interface $T_S \to 0$, the zero bias conductance vanishes as $G_{SN} \sim T_S^2$ for ballistic junctions, as shown by (2.41), whereas $G_N \propto T_S$. It is shown, however, that if $T_N \approx T_S$, then $G_{SN} \sim G_N$. This effect can be understood on the basis of multiple scatterings between the two barriers, which substantially increases the probability of Andreev reflection on the SN interface in spite of the presence of the tunneling barrier. For quantitative results, we take the normal state and zero bias conductance in the tunneling limit ($T_N, T_S \to 0$):

$$G_N = \frac{2e^2 N}{\hbar} \left( T_N^{-1} + T_S^{-1} \right)^{-1}$$

(2.47)
2.3. SUPERCONDUCTOR–NORMAL METAL JUNCTIONS

Figure 2.15: The signature of coherent diffusive backscattering in an Al-Cu constriction is the nonmonotonic temperature dependence of the zero bias conductance, denoted by reentrant conductance. In order to dismiss the huge background of supercurrent, the conductance through the normal lead of the junction has been measured. Taken from [82].

which is the result of simply adding the resistance of the two junctions. In contrast, in the zero bias limit coherent summing of the multiple modes acquiring random phase shift between the interfaces is necessary. The result is [80]:

$$G_{SN} = \frac{2e^2N}{\hbar} \frac{T_N^2 T_S^2}{(T_N^2 + T_S^2)^{3/2}} \quad (2.48)$$

exhibiting a clear peak around $T_N \approx T_S$ (Fig. 2.16a). For a given $T_S$, the maximum is achieved if $T_N = \sqrt{2}T_S$, where $G_{SN} \propto T_S$ instead of $G_{SN} \propto T_S^2$ as in the BTK result. The partial lifting of the tunnel barrier was first observed experimentally by Kastalsky et al. on a Nb-n$^+$InGaAs junction [79] (Fig. 2.16b).

Decoherence effects

It is apparent, that the characteristic path length in systems described by Fig. 2.14a is of the order of $L$. Hence, coherent summing for different paths, i. e. coherent summing of the scattering matrices is justified only if

$$L \ll l_\phi = \sqrt{D\tau_\phi} \quad (2.49)$$

holds. Here, the dephasing time $\tau_\phi$ is characteristic of different processes as discussed below.

The dephasing time can be rewritten as $\tau_\phi \approx \hbar/\Delta E$, where $\Delta E$ is the typical smearing of the energy levels. For dephasing due to finite temperature, $\Delta E \approx k_B T$, hence

$$L_T = \sqrt{\frac{\hbar D}{k_B T}} \quad (2.50)$$
is the associated length scale and $L \leq L_T$ is a necessary condition to observe coherent effects in the conductance. Similarly, finite bias through the junction destroys coherence as well within a typical length of

$$L_V = \sqrt{\frac{\hbar D}{2eV}}. \quad (2.51)$$

This is attributed to the $\Delta E = 2eV$ energy difference of the quasiparticles involved in the Andreev reflection process. For a specific system characterized by a typical $L$ length, (2.50) and (2.51) define a temperature $T^*$ and a bias voltage $V^*$ below which one can observe coherent interference effects in the conductance. It should be noted, that size of the system is often characterized by the Thouless energy:

$$E_t = \frac{\hbar D}{L^2}. \quad (2.52)$$

Using this notation phase coherence is preserved if $E_t \ll k_B T$ and $E_t \ll 2eV$. It follows from this discussion, that coherent backscattering is a correction in the conductance near zero bias at low enough temperatures (Fig. 2.16b) [79,83,84].

Finally, we note that since Andreev reflected quasiparticles belong to different spin subbands, their energy levels split by $\Delta E = g\mu_B B$ in a finite $B$ magnetic field. In a ferromagnetic metal, the $B_{\text{ex}}$ exchange field is the source of dephasing, related to the Curie temperature $g\mu_B B_{\text{ex}} \sim k_B T_c$ in the low temperature limit. Thus, the dephasing length for a ferromagnetic metal can be estimated as:

$$L_{\text{FM}} = \sqrt{\frac{\hbar D}{k_B T_c}}. \quad (2.53)$$
As typically measurements are performed in cryogenic environments, for a strong ferromagnet $T_c \gg T$ holds, resulting in $L_{FM} \ll L_T$. This argument supports the observation of fast decoherence in ferromagnets suppressing interference effects in the conductance.

2.4 Superconductor – ferromagnetic metal (SF) junctions

Previously we mostly discussed the electrical transport through an SN junction consisting of a nonmagnetic metal and a superconductor. In this section we include a ferromagnetic metal in the normal side and discuss two models to describe the influence of a finite spin polarization on the electronic transport. Here, we only consider itinerant ferromagnets in which charge carriers are not localized ($l_m \gg \lambda_F$), therefore a Fermi surface exists at least for one of the spin subbands.

2.4.1 Superconducting tunneling spectroscopy

Let us consider a superconducting – normal metal tunnel junction. In the tunnel limit, only quasiparticle transport is taken into account, therefore the differential conductance is:

$$G(V) = \frac{\partial I(V)}{\partial V} = \frac{e^2}{h} T \rho_N(\varepsilon_F) \int_{-\infty}^{\infty} d\varepsilon \rho_S(\varepsilon) \left(-\frac{\partial f_0(\varepsilon + eV)}{\partial \varepsilon}\right)$$

with the quasiparticle density of states in the normal metal and the superconductor:

$$\rho_N(\varepsilon) = \text{constant} = \rho_N(\varepsilon_F), \quad \rho_S(\varepsilon) = \rho_0(\varepsilon_F) \frac{|\varepsilon|}{\sqrt{\varepsilon^2 - \Delta^2}}$$

In magnetic field, the quasiparticle spectrum in the superconductor splits with the Zeeman energy $2\mu_B B$ (Fig. 2.17a). In this case we have to consider the tunneling conductance in each spin subband:

$$G(V) = \frac{e^2}{h} T \rho_\uparrow(\varepsilon_F) \int_{-\infty}^{\infty} d\varepsilon \rho_{S\uparrow}(\varepsilon) \left(-\frac{\partial f_0(\varepsilon + eV)}{\partial \varepsilon}\right) + \frac{e^2}{h} T \rho_\downarrow(\varepsilon_F) \int_{-\infty}^{\infty} d\varepsilon \rho_{S\downarrow}(\varepsilon) \left(-\frac{\partial f_0(\varepsilon + eV)}{\partial \varepsilon}\right)$$

(2.56)

neglecting spin-flip scattering in the interface. If the metallic side is ferromagnetic, so that $\rho_\uparrow(\varepsilon_F) \neq \rho_\downarrow(\varepsilon_F)$, (2.56) has a characteristic asymmetry, plotted in Fig. 2.17c and Fig. 2.17d. [85] It is notable, that in general $T_\uparrow \neq T_\downarrow$ thus that this method measures the tunneling spin polarization

$$P_T = \frac{\rho_\uparrow(\varepsilon_F) T_\uparrow - \rho_\downarrow(\varepsilon_F) T_\downarrow}{\rho_\uparrow(\varepsilon_F) T_\uparrow + \rho_\downarrow(\varepsilon_F) T_\downarrow}$$

(2.57)
instead of (2.29).

The applied magnetic field should be smaller than the critical magnetic field of the superconductor, so that the superconducting ordering does not collapse. Also, in order to provide a reasonable fitting, the splitting should be as large as possible, therefore usually $\mu_B B \lesssim \Delta$ relation is used. Such magnetic field has no influence on the ferromagnet, since usually $\Delta \ll \mu_B B_{ex}$.

### 2.4.2 Andreev reflection in superconductor – ferromagnet junctions

#### The modified BTK theory of ferro-supra junctions

In the BTK theory it is assumed, that the normal side of the junction is not spin polarized. However, in case of a half-metal (where the Fermi level crosses only one of the spin subbands) Andreev reflection is inhibited because of the spin constraint between the incoming electron and reflected hole. In order to characterize realistic ferromagnets with arbitrary $\rho_\sigma(\varepsilon_F)$, we consider the current through the interface as a sum of a polarized and unpolarized part [34,86]:

$$I = I_\uparrow + I_\downarrow = 2I_\downarrow + (I_\uparrow - I_\downarrow) = (1 - P_c)I_{\text{unpol}} + P_c I_{\text{pol}}.$$  \hfill (2.58)

using the notation

$$P_c = \frac{I_\uparrow - I_\downarrow}{I_\uparrow + I_\downarrow}. \hfill (2.59)$$

Here, only the second $I_{\text{pol}}$ component carries spin polarization, whereas the first $I_{\text{unpol}}$ term is determined by (2.38). In order to calculate $I_{\text{pol}}$, we set $A_{\text{pol}}(E, Z) = 0$ for the probability of the Andreev reflection. The quasiparticle reflection and transmission amplitudes can be calculated based on the assumption that their ratio is preserved:

$$\frac{B_{\text{unpol}}}{1 - A_{\text{unpol}} + B_{\text{unpol}}} = \frac{B_{\text{pol}}}{1 - B_{\text{pol}}} \hfill (2.60)$$
leading to
\[ B_{\text{pol}} = \frac{B_{\text{unpol}}}{1 - A_{\text{unpol}}} \] (2.61)
making it possible to evaluate (2.38) for the polarized current. The net current is provided by (2.58) with \( P_c \) as an additional parameter. By evaluating the zero bias conductance at zero temperature and a perfectly transparent junction, we get
\[ \frac{G(V = 0)}{G_N} = 2(1 - P_c) \] (2.62)
in agreement with the scheme of the vanishing Andreev reflection amplitude as \( P_c \) increases (Fig. 2.18a). This property makes it possible to deduce \( P_c \) by evaluating (2.62) from measured data. However, for more realistic cases, when finite temperature and finite backscattering (Fig. 2.18b-2.18d) are included, the full \( G(V) \) curve is to be evaluated so that \( P_c \) and \( Z \) could be simultaneously obtained. This goal, however, can only be achieved if the barrier backscattering is not too high, otherwise the differential conductance curve is not sensitive to the value of spin polarization. Thus, high transparency \( Z \to 0 \) junctions are preferred for investigating ferromagnetism.

The above scheme, based on the renormalization of the quasiparticle processes, is not well founded in terms of the scattering matrix theory, and is shown to violate the current conservation through the interface for arbitrary \( Z \) and bias voltage. A more strict model for calculating the spin polarized part of the current is given by Mazin et al. [87], who considered the Andreev reflected quasiparticle as an evanescent wave near the interface for the spin polarized part of the current. Then, the wave matching equations are solved similarly to the original BTK model and finally the total current is written as (2.58). It has been shown that although the second calculation yields to a different \( G(V) \) curve with some discrepancies at \( eV \approx \Delta \), at experimentally reasonable temperature values the results are essentially indistinguishable in measurements [88]. Moreover, at \( Z \to 0 \) this difference vanishes.

The Hamiltonian description of SF junctions

A microscopic theory of the electronic transport through a SF interface is based on the following model Hamiltonian [89,90]:
\[ \mathcal{H} = \mathcal{H}_L + \mathcal{H}_R + \sum_\sigma \tau_\sigma c_{L\sigma}^\dagger c_{R\sigma} + \tau_\sigma^* c_{R\sigma}^\dagger c_{L\sigma}. \] (2.63)
Here \( \mathcal{H}_L \) and \( \mathcal{H}_R \) denotes the Hamiltonian of the uncoupled left and right electrodes, respectively. Specifically for SN junctions \( \Delta_L = 0 \) and \( \Delta_R = \Delta \), i. e. the superconducting order parameter exhibits a step at the interface. Note, that in this model, spin dependent hopping elements \( \tau_\uparrow \) and \( \tau_\downarrow \) are defined [90] and are related to the elements of the normal state transmission matrix
\[ T = \begin{bmatrix} t_\uparrow & 0 \\ 0 & t_\downarrow \end{bmatrix} \] (2.64)
as \( t_\sigma = \frac{2\tau_\sigma}{W} \) with \( W \) being the bandwith of the quasiparticle spectrum.

The \( A_\sigma \) and \( B_\sigma \) Andreev and normal reflection amplitudes are then calculated using nonequilibrium Green function methods and the current in the corresponding spin subband can be evaluated similarly to the BTK form (2.38) [37]:

\[
I_\sigma(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE \left( f_0(E - eV) - f_0(E) \right) \left( 1 + A_\sigma(E) - B_\sigma(E) \right)
\]

and the total current is \( I = I_\uparrow + I_\downarrow \). If no spin polarized transport is involved, so that \( T_\uparrow = T_\downarrow = T \), the resulting conductance is the same as the BTK result with \( T = (1 + Z^2)^{-1} \). On the other hand, for arbitrary \( T_\uparrow \) and \( T_\downarrow \) values it cannot be mapped to the modified BTK calculations presented earlier. For this model, the spin

Figure 2.18: Differential conductance curves for the modified BTK theory for various \( P_c \) values. (a) and (b) A perfectly transparent junction at zero temperature, and at \( \frac{k_B T}{\Delta} = 0.25 \), respectively. (c) and (d) Finite \( Z \) values demonstrating the impact of \( P_c \) with increasing \( Z \).
polarization of the current through the interface is:

\[ P_H = \frac{T_\uparrow - T_\downarrow}{T_\uparrow + T_\downarrow} \]  

(2.66)

Figure 2.19: Simulated \(G(V)\) curves for the Hamiltonian transport model of SN junctions of different \(P_H\) spin polarization (2.66). The transmission for the majority band is \(T_\uparrow = 1\) (a) and \(T_\uparrow = 0.5\) (b).

In order to make a direct comparison to the modified BTK model, differential conductance curves for the same spin polarization values shown in Fig. 2.18 are plotted in Fig. 2.19. The \(T_\uparrow = 1\) and \(T_\uparrow = 0.5\) values are also chosen in correspondence to \(Z = 0\) and \(Z = 1\) (2.40). It is apparent, that at finite temperature only a small discrepancy is visible near \(|eV| = \Delta\). The similar simulated curves for the corresponding \(P_c\) and \(P_H\) spin polarization values provide a strong argument that the two models catch the same aspect of spin polarized transport despite their fundamentally different approach. Nevertheless, in order to compare their reliability for actual measurements, only independent fitting and subsequent comparison can provide unambiguous proof as discussed in Chapter 4.

Finally, we note that we only addressed SF junctions with a single \(T_\uparrow\) and \(T_\downarrow\) value. This condition might be fulfilled in single atomic junctions, if only a single propagating channel is present. However Andreev reflection measurements are typically performed utilizing larger SF junctions, where numerous transmitting channels are present. Nevertheless, based on (2.22), one can reformulate the linear conductance:

\[ G = \frac{e^2}{h} M_\uparrow \left( \bar{T}_\uparrow + \frac{M_\downarrow}{M_\uparrow} \bar{T}_\downarrow \right) = \frac{e^2}{h} M_\uparrow (\bar{T}_\uparrow + \bar{T}_\downarrow^*) . \]  

(2.67)

Here, \(\bar{T}_\downarrow^*\) is defined as an effective transmission in which the reduced number of propagating channels is included, so that \(\bar{T}_\uparrow > \bar{T}_\downarrow^*\). It is therefore instructive to address spin
polarized transport by introducing spin dependent transmission eigenvalues even if the number of propagating channels is large, so that they cannot be described by a single $T_\sigma$ transmission value.

**Limiting factors of analysis**

An essential part of the theoretical description of a ferromagnet – superconductor junction is the suppression of the Andreev reflection amplitude due to the spin ordering. Hence, for analysis of experimental data, it is preferred to have a low barrier junction, whereas in the tunneling limit spin polarized and unpolarized transport cannot be distinguished as Andreev reflection is suppressed regardless of the spin polarization.

Even for reasonably good transmission a systematic decrease of the detected spin polarization with decreasing junction transparency was observed by Strijkers et al. [86], and later explained by Kant et al. [91]. In their model the transmission probability of a scattering region of a finite thickness $l$ is calculated:

$$T = \frac{1}{1 + \frac{L}{l_m}(1 - \Psi)}$$  \hspace{1cm} (2.68)

where $l_m$ is the mean free path of the charge carriers and $\Psi$ the probability of forward scattering. This equation provides a result which can be interpreted within the framework of BTK. Specifically, using (2.40), we find

$$Z^2 = (1 - \Psi) \frac{l}{l_m}.$$  \hspace{1cm} (2.69)

Even though $Z$ was originally the dimensionless strength of a specular barrier on the interface, it can be defined for a finite barrier thickness as well. The physical picture of the decaying spin polarization is then based on a finite spin-flip probability $\alpha$ for each scattering process within the scattering region. By summarizing for all paths of multiple scatterings, it can be shown that [91]:

$$P = P_0 e^{-2\alpha\Psi Z^2}.$$ \hspace{1cm} (2.70)

This result further stresses the necessity of using junctions of as low barrier strength, i.e. as high transmission, as possible. In order to gain reliable spin polarization value from experimental data, it is sometimes even necessary to plot $P(Z)$, and by fitting it against (2.70), to obtain $P_0$.

It is frequently observed in the experiments, that the $G(V)$ curve is smeared compared to what is expected from the $\Delta(T)/k_B T$ ratio. Such deviation is usually explained on the basis of a finite quasiparticle recombination time, $\tau_r$, usually being defined as [92]:

$$\Gamma = \frac{\hbar}{\tau_r}.$$ \hspace{1cm} (2.71)
which is directly comparable to the superconducting ordering parameter $\Delta$. The corresponding quasiparticle density of states is (Fig. 2.20):

$$\rho(E) = \left| \text{Re} \left( \frac{E + i\Gamma}{\sqrt{(E + i\Gamma)^2 - \Delta^2}} \right) \right| \rho(\varepsilon_F),$$

leading to a subgap density of states of

$$\rho(E = 0) = \frac{\Gamma}{\sqrt{\Gamma^2 + \Delta^2}} \rho(\varepsilon_F).$$

(2.73)

Figure 2.20: The superconducting density of states for different $\Gamma$ parameters (2.72).

Superconducting tunneling spectroscopy showed that (2.72) gives a good agreement with experimental data for superconductors in the strong coupling limit [92], granular superconductors [93], and HTC materials [30]. Despite the good agreement between the phenomenological picture and experimental data on many distinct materials, there is no general microscopic picture of the broadening. Applied theories include structural defects for HTC superconductors, enhanced inelastic scattering rate, as well as fluctuations of two level systems [94]. It is important to note, that if $\Gamma \approx \Delta$, the superconductivity is destroyed, therefore it is unphysical to relate observed features to the quasiparticle broadening, if $\Gamma > \Delta$ follows from the experimental data.

By evaluating the coherence factors, the BTK calculations can be extended for the case of (2.72). [30,95] A notable result is the smearing of the sharp features at $eV = \Delta$ (Fig. 2.21a). For spin polarized transport, the subgap conductance shows less variation compared to (2.62) (Fig. 2.21b). Hence the error of the recovered spin polarization increases drastically if this additional parameter is included. It is therefore essential to have junctions with well-developed superconductivity which can be achieved by the proper choice of materials as well as proper surface treatment on the boundary of the superconductor and the normal metal.
2.5. PREPARATION OF HETEROJUNCTIONS

In this section we will focus on the experimental development of creating heterojunctions, i.e. point contacts between two different materials in which the transport through an SN interface can be investigated. Possible realizations of such junctions are illustrated in Fig. 2.22 and will be discussed in detail below.

Figure 2.21: (a) Differential conductance curves for different barrier strength values at finite temperature and $\Gamma = 0.3\Delta$. (b) Spin polarized transport in the presence of a finite $\Gamma$. Note the reduced scale of the conductance as compared to Fig. 2.18c.

2.5 Preparation of heterojunctions

In this section we will focus on the experimental development of creating heterojunctions, i.e. point contacts between two different materials in which the transport through an SN interface can be investigated. Possible realizations of such junctions are illustrated in Fig. 2.22 and will be discussed in detail below.

Figure 2.22: Three possible ways to create point contacts between different materials. (a) Standard lithography procedure, which makes rather complex structures possible. The schematic view of a SININ junction is taken from [96]. (b) Creating small holes using reactive ion etching through membranes [97]. (c) Creating the junction in situ, by touching the sample surface with a separate tip.
2.5. PREPARATION OF HETEROJUNCTIONS

2.5.1 Lithography

One method to create mesoscopic point contacts is to prefabricate the constriction \textit{ex situ}. Controlled fabrication of nanojunction between a superconductor and an arbitrary metal is possible with standard electron beam and photolithography techniques. Such point contacts generally exhibit excellent mechanical stability when cooled down, thus quite compact and simple sample holder designs can be used in this case. Using proper design considerations, one could even fabricate more complicated devices than a simple SN junction, e. g. double barrier SININ constrictions [96] that can be designed to be either in the reflectionless tunneling or the reentrant conductivity regime. However, these structures are usually large compared to the elastic mean free path, i. e. diffusive transport is implied.

In order to reach the ballistic limit, a commonly used technique is to create a nanohole through a suitable material, e. g. Si$_3$N$_4$. This can be achieved by defining a pit by standard lithography processes, and then opening it by reactive ion etching techniques [37,97,98]. The typical hole size is in the 3 nm...20 nm range making this method suitable to reach the ballistic regime. The metals are then evaporated on each side of the membrane, creating the junction (Fig. 2.23).

![Diagram of the creation of superconducting – ferromagnetic junction via a nanohole etched through a Si$_3$N$_4$ membrane [37,98].](image)

Point contacts created by this method exhibit good mechanical stability despite their small conducting area. However, the exact diameter of the junction cannot be controlled, and cannot be observed directly, hence it can only be deduced from the resistance of the contacts, using the Wexler equation (2.9). This fabrication process does not allow to investigate many distinct junctions, making statistical analysis rather inconvenient.

2.5.2 Tip-sample geometry

A viable approach to create metallic point contacts is to gently touch a sample surface with a sharpened tip. This setup was first used in 1976 by Yanson and Shalov [99], to directly measure phonon modes in metals (Fig. 2.24a). [100] Later, the first experimental justification of the BTK theory was also performed by this technique [27]. The
development of the scanning tunneling microscope (STM) in 1986 [101] provided more sophisticated nanopositioning tools such as piezo actuators which replaced mechanical fine tuning of the point contact.

Further development has enabled to achieve a continuous tuning of the junction from the tunneling to the contact regime [102]. Thus, using this method, one can create metallic junctions down to the single atomic regime, where full quantum mechanical description of the point contact is necessary. Moreover, by periodically retracting the tip and then touching the sample again at a different lateral position, many distinct junctions can be investigated, making a statistical analysis possible.

![Figure 2.24](image)

**Figure 2.24:** (a) An early point-contact sample holder design taken from [100] (b) A state of the art low temperature STM setup from [103].

A drawback of this approach is the high demand on the mechanical stability of the measurement setup. Nevertheless, at constant temperature and magnetic field, modern STM designs are capable of reaching a lateral drift down to 0.1 nm/h [103]. However, such setups are not well suited for continuous temperature or magnetic field sweeps due to the disturbing influence of thermal expansion or magnetostriction.

### 2.6 Novel memory concepts

Even though the point contact geometry discussed above is typically used in fundamental research, such schemes have greatly contributed to the development of nanoelectronics. As it will be demonstrated later, our point contact Andreev reflection measurements were capable of addressing the details of local electronic transport both
in nanoscale ferromagnetic structures, similar to those applied as spin valves, and the Ag$_2$S-based memristive systems. In this section, first we discuss earlier experiments and theoretical work associated with the physics of spin valves, and then we briefly introduce the field of memristive systems, focusing on the Ag$_2$S-based cells.

2.6.1 Spin valves

Giant magnetoresistance

The spin valve trilayer structures typically consist of two ferromagnetic thin films (FM) and a nonmagnetic spacer layer (N) in between (Fig. 2.25a), however, multilayer structures with many alternating ferromagnetic – nonmagnetic sequences also exist. By measuring the influence of the in-plane magnetic field on the resistance, a variation typically in the order $\Delta R/R \sim 1\% \ldots 10\%$ was found. This magnetoresistance is orders of magnitude higher than that of single layer ferromagnets. Moreover, the special shape and hysteretic effect of the resistance – magnetic field plot revealed the role of the relative magnetisation direction (parallel – antiparallel) of the FM films.

![Figure 2.25: (a) Spin valve structure in the current perpendicular to the plane (CPP) geometry. (b) The magnetic field evolution of the resistance of a spin valve device exhibiting the GMR effect $\Delta R = R_{AP} - R_P$. Adopted from [6].](image)

The giant magnetoresistance has been discovered by A. Fert et al. [7] and P. Grünberg et al. [8], both awarded with a Nobel prize in physics in 2007. This effect can be phenomenologically explained on the basis of the spin filtering in each FM layer causing an enhanced spin scattering on the FM-N interface if the FM layers are antiparallel aligned. Hence, the resistance of the device increases [104] with respect to the parallel magnetic orientation [105].

We note that here we only discuss the GMR effect for the current flowing perpendicular to the plane (CPP) of the layered structure (Fig. 2.25a). However, the GMR effect was first observed in the current in plane (CIP) scheme [7, 8], for which no sophisticated nanopatterning is necessary. Later, it was experimentally demonstrated by
2.6. NOVEL MEMORY CONCEPTS

W. P. Pratt et al. [105], that the CPP geometry is more appropriate to achieve large relative resistance changes.

**Role of the spin diffusion length**

The simplest scheme of the spin valve assumes that no spin-flip scattering occurs in the N layer, so that the filtered electronic spins traverse unaltered between the FM layers. This is indeed the case if the N layer thickness \( d \) is much smaller than the spin diffusion length \( l_s \). If, however, \( d \gtrsim l_s \), the spin memory is lost and the amplitude of the magnetoresistance is suppressed. For the CPP geometry, this decay was first addressed by T. Valet and A. Fert [9], who showed that the characteristic length scale is the spin diffusion length of the nonmagnetic layer:

\[
\frac{\Delta R}{R} \propto \exp(-d/l_s),
\]

where \( d \gtrsim l_s \) is the thickness of the spacer layer. Based on this characteristic cutoff, the spin valve scheme has become a frequently used geometry to study the decay of spin information in metals [6, 106], multilayer structures [106], as well as carbon nanotubes [10]. Typical measurement data for simple metals at \( T = 4.2 \text{K} \) are shown in Fig. 2.26 [106].

![Figure 2.26](image)

*Figure 2.26: The influence of the spacer layer thickness \( t \) on the amplitude of the GMR effect. The specific materials investigated are shown in the figure. The plot was taken from [106].*

**The MRAM**

The intriguing concept to use the spin valve structure (Fig. 2.25a) as a memory cell led to the development of the magnetic random access memory (MRAM). The
parallel and antiparallel orientation of the FM layers can serve as bit “0” and “1”, respectively, and the readout is performed by measuring the resistance of the device. In fact, this scheme has already been used in hard disk drives (HDD), where the readout of the data stored in magnetic domains on the rotating plate is done by a spin valve device [107,108]. The stray field of the domains determines the orientation of one of the FM layers, whereas the other one is pinned. Readout of the magnetic information is then performed by exploiting the GMR effect.

![Diagram](image)

Figure 2.27: (a) Spin valves organized in a crossbar architecture. Note that supplementary semiconductor elements are not shown for simplicity [109]. (b) An individual spin valve together with associated writing circuitry consisting of two perpendicular pathways of current [110].

The more advanced concept of integrating many spin valves in a crossbar architecture (Fig. 2.27a) has proved to be a viable alternative [109,111]. Such devices have already been commercialized [110] using a write mechanism that utilizes the induced magnetic field of the current flowing above the device (Fig. 2.27b). However, due to the complicated addressing mechanism and crosstalk effects, these circuits are still of limited storage capacities.

Further developments made writing each bit possible without any auxiliary circuitry possible. This is achieved by exploiting the spin transfer torque (STT) effect, where the spin polarized electronic current expresses a torque on the magnetization of the ferromagnetic layers. This mechanism, observable at high current densities, was first proposed by J. C. Slonczewski [112], and identified by Tsoi et al. [113]. Using STT for writing, each memory cell is a two-terminal device that can be written by a large amplitude current pulse, whereas the readout is performed at a low bias utilizing the GMR effect [114].
2.6. NOVEL MEMORY CONCEPTS

2.6.2 Resistive switching materials

Resistive switches recently gained attention as a possible route for novel solid state data storage and even novel computer architectures. Despite the rather coherent phenomenological description of such devices, there are many physical and chemical processes which may lead to a persistent change in the device resistance. Here, we first classify the resistive switching materials by their apparent $I-V$ characteristics, then discuss the mathematical model of the so-called memory-resistor (memristor). Finally, the specific memristive system addressed in this thesis will be discussed in detail.

Classification of the resistive switching effects

The first experimental demonstration of the memristive behavior in a Pt-TiO$_2$-Pt multilayer structure in 2008 [15] triggered significant theoretical and experimental work in order to classify the switching mechanisms observed earlier.

The most apparent classification is based on the voltage polarity for the transitions [16]. The switching is unipolar if the process does not depend on the polarity of the voltage bias through the device (Fig. 2.28a). In such systems, the OFF-ON transition is aided by an external current compliance (c.c.), whereas no such limiting is included for the ON-OFF switching. To operate unipolar switches, only bias voltages of a single polarity are needed, hence transitions for both polarities in Fig. 2.28a merely demonstrates the symmetry of the device. Notable examples are those structures in which Joule heating of the junction is involved, such as phase change memory cells [115] and thermochemical devices based on the phase transition of VO$_2$ [116].

![Figure 2.28](image-url)

Figure 2.28: The classification of resistive switching mechanisms after [16]. (a) $I-V$ curve of an unipolar switch, featuring a current compliance (c.c.) regime necessary in the driving circuit for the OFF-ON transition. (b) The bipolar switch, where the ON-OFF and OFF-ON transitions only occur at opposite polarity, thus bipolar driving circuit has to be used.
In contrast to the unipolar switching mechanisms, for bipolar switching (Fig. 2.28b) the ON-OFF transition takes place only in the opposite polarity as the OFF-ON transition [16]. Here, typically a bias-driven electrochemical reaction takes place inside the cell, resulting in the change of the resistance. A possible process is the local change of the stoichiometry usually referred to as valence change mechanism (VCM) [117]. Alternatively the diffusion and subsequent dissolution of one of the electrode materials can be exploited (electrochemical metallization mechanism, ECM) [17]. In contrast to unipolar mechanisms, which can, in principle, occur in perfectly symmetrical devices, bipolar switches must have an inherent asymmetry, that can be reached e. g. via electroforming the cell under a certain bias polarity, or by using different electrode materials.

Based on the apparent pinched hysteresis loop in the $I-V$ characteristics of bipolar resistive switches, the nonlinear two-pole element memristor is often used to describe them in circuit theory [15]. Even though such correspondence discards fine details of the actual device, e. g. abrupt changes in the resistance, it eases simulation of novel applications, such as neural networks [118].

Mathematical description of memristors

In nonlinear circuit theory, the term memristor is defined by the following equation [14]:

$$V(t) = M(Q)I(t).$$

(2.75)

Here the $M(Q)$ memristance is an arbitrary function of the charge that has passed through the device. This feature introduces a memory effect, since instead of a direct voltage or current dependence, the characteristics of the system depends on its history. In order to demonstrate how this feature results in the pinched hysteresis loop, we consider a system with $M = M_0 + M_1Q$ under a sinusoidal drive of $I(t) = I_0 \cos(\omega t)$. The resulting $I-V$ curve is shown in Fig. 2.29, exhibiting two distinct zero bias resistance values:

$$R(V = 0) = R_0 \pm \Delta R = M_0 \pm \frac{M_1 I_0^2}{\omega}$$

(2.76)

making this model appropriate to describe a resistive memory which can be altered with a voltage pulse of

$$V_{set} \approx \sqrt{\frac{\Delta R \omega M_0^2}{2M_1}}$$

(2.77)

and read with a voltage of $V_{read} \ll V_{set}$ in order not to alter the state with the reading operation.

This simple model however fails to describe many properties of actual realizations of resistive switches, therefore a more broad class of devices were defined as memristive systems by the following equations [119, 120]:

$$I(t) = M^{-1}(X,V,t)V(t)$$

(2.78)

$$\dot{X} = f(X,V,t)$$

(2.79)
2.6. NOVEL MEMORY CONCEPTS

Figure 2.29: Typical characteristics of a memristor described by (2.75) under sinusoidal current bias. Left: the time evolution of the current, accumulated charge and voltage respectively. Right: the $I-V$ curve of the system.

describing $M$, the memristance as a function of an internal state variable, $X$, whose time evolution is described by the second equation. Note, that using the notations of (2.75), $X = Q$. In (2.79), however, it can be either an arbitrary function of $Q$, or any other physical property of the system. Notable examples are the absolute temperature ($X = T$) for a model circuit containing a self-heating thermistor [119], or the tunnel gap ($X = d$) separating two conducting parts for the TiO$_2$-based resistive switches [121].

Despite the extreme variety of physical systems that can be described within the above framework, applied research of the topic did not start until the demonstration of both fast write operation (on the ns scale) and long data retention (more than 10 years). This is usually possible by exploiting an activated process changing the electronic conductivity of the cell. Notable examples are the drift of the oxygen vacancies locally doping the semiconductor matrix in TiO$_2$ [121], or the ionic conductivity in chalcogenide compounds [24] which is discussed below in detail.

The Ag-Ag$_2$S system

The structure of a typical memory element based on an electrochemically active volume capable of changing its resistance is sketched in Fig. 2.30. An important feature of such devices is the inherent asymmetry because of the different electrode materials. One of the electrodes, denoted by electrochemically active electrode can dissolve in the insulator layer effectively changing the conductance of the device. Frequently used metals are Ag and Cu.

The other electrode, however, is electrochemically inert, meaning that it is not influenced by the change of the bias voltage through the cell. Many transition metals including Ti, Pt, Ir or W are demonstrated to perform well as the inert electrode.

A very broad range of elements and compounds have been investigated as the electrochemically active region, such as Ag$_2$S [19], Cu$_2$S [122], WO$_3$ [123], SiO$_2$ [124],
amorphous Si [21], and conducting polymers [125].

From now on, we restrict ourselves to the discussion to the properties of the Ag-Ag$_2$S-Me system, where Me is an electrochemically inert transition metal or compound. Here the resistive switching is governed by the solid state electrochemical reaction taking place inside the Ag$_2$S layer and the Ag-Ag$_2$S boundary:

$$Ag^{+}(Ag_2S) + e^- \rightleftharpoons Ag_{(metal)}$$ \hspace{1cm} (2.80)

as follows in detail (Fig. 2.31). The OFF-ON transition in the cell happens if large enough positive voltage is applied to the electrochemically active Ag electrode:

(i) First, metallic silver dissolves in the Ag$_2$S layer:

$$Ag_{(metal)} \rightarrow Ag^{+}(Ag_2S) + e^-$$ \hspace{1cm} (2.81)

(ii) the Ag$^+$ cations migrate inside the solid state electrolite driven by the external electric field

(iii) The cations are reduced and crystallized on the surface of the inactive electrode. This process described by the reaction:

$$Ag^{+}(Ag_2S) + e^- \rightarrow Ag_{(metal)}$$ \hspace{1cm} (2.82)

The channel of Ag atoms now shunts the semiconducting matrix, reducing the resistance of the cell.

For thick Ag$_2$S layer which can considered bulk, it was shown that the OFF-ON transition time obeys the Arrhenius law [24]:

$$t_{sw} \propto e^{-\frac{E_a}{k_BT}}$$ \hspace{1cm} (2.83)

proving that processes (i),(ii) and (iii) are thermally activated in the semiconducting Ag$_2$S layer. Multiple $E_a$ activation energies ranging from 0.58 eV to 1.32 eV were found [24] showing that the rate limiting process for the OFF-ON transition can be any of the three discussed above depending on the external bias driving conditions.

In contrast to bulk samples, atomically thin Ag$_2$S films enclosed between Ag layers are presumed to exhibit metallic conductance due to a structural relaxation [126,127]. The zigzag arrangement of Ag atoms shown in Fig. 2.32a is predicted by ab initio
2.6. NOVEL MEMORY CONCEPTS

Figure 2.31: The representation of the electrochemical reaction cycle (2.80). The bottom configuration corresponds to the OFF state, whereas the top configuration is the ON state. On the left and the right side, bias voltage is applied with the polarity shown.

Figure 2.32: (a) Top: the stable arrangement of Ag (yellow) and S (cian) atoms in a thin Ag$_2$S layer sandwiched between two bulk Ag electrodes. Bottom: the colorscale plot of the electronic density clearly showing the chain of Ag atoms. (b) The transmission through the layer and the corresponding density of states for the unrelaxed and relaxed Ag$_2$S layer, respectively. Taken from [126].

calculations, resulting in a finite density of states, hence finite transmission at the Fermi level (Fig. 2.32b).

It should be stressed that in actual devices symmetric electrode configuration used in this model is not favorable. However, such relaxation might occur in thin Ag$_2$S films created on the top of a silver metallic layer as well. While earlier experiments have usually been performed on thick Ag$_2$S layers ($\gtrsim 100$ nm, see e. g. [128]), where thermally activated transport has been demonstrated, investigation of thin, metallic
films might open new opportunities for creating true nanoscale memory cells.
Chapter 3

Experimental techniques

In this chapter, the design and assembly of the measurement system used during my Ph.D. work is presented. The experimental setup, employing the tip-sample approach, has been exclusively developed at the Department of Physics of the Budapest University of Technology and Economics. The careful mechanical and electronic design and construction were essential to obtain the experimental results discussed in my thesis, therefore setting up the measurement system was an essential part of my PhD work. The earlier mechanical controllable point contact setups developed in our department [129] provided the solid background of knowledge which was vital for me to successfully build the measurement system discussed below.

First, the mechanical design of the setup will be presented. The design goal was to create stable nanometer scale junctions between a tip and a sample. Proper stability had to be reached in order to measure the $I-V$ characteristics of such junctions.

The measurement electronics was designed keeping low noise level in mind. Since the main purpose of the system is to measure the nonlinearity of the differential conductance curves on the scale of the superconducting gap, the goal was to achieve a substantially lower voltage noise level.

Finally, the measurement control system is shown. In order to conveniently control the parameters of the ongoing experiment, a highly automated control software was developed. To provide the possibility of suitting the control program for different kind of measurements, a highly modular design was followed.

3.1 Mechanical design

The measurement setup follows the tip-sample approach, i. e. the point contact is created by gently touching the sample surface by a sharp tip. This provides the possibility to make junctions between different types of materials, however care must be taken to prevent the contamination of the sample or the tip surface. This scheme was first used in the pioneering point contact experiments of Yanson et al. [99], who performed the measurements with a solely mechanical tuning of the junction. A similar setup was used by Blonder and Tinkham [27] to experimentally confirm the BTK theory.
of superconductor – normal metal junctions.

Later, actuators exploiting the piezoelectric effect emerged [130], enable positioning with sub-Angström resolution. Furthermore, such actuators are controlled purely electronically, which makes them rather convenient to use. Our custom-built measurement setup also includes piezoelectric actuators for fine tuning of the contact as discussed in detail below.

### 3.1.1 The sample holder

The assembly of the sample holder is shown in Fig. 3.1. The parts at the top are at ambient conditions, whereas the bottom is immersed into liquid helium to provide the necessary cooling. In order to reduce the heat load to the helium bath, stainless steel tubes (I,II) were used and radiation shields (III) were also fitted. Apart from these tubes, most of the assembly is made of brass as it is easy to machine, while it is reasonably stiff. Another favorable property of brass is its good electrical and heat conduction that aids thermalization.

The sample holder is designed to fit either in a liquid helium transport vessel (RH100) or in an Oxford Instruments cryostat, where measurements under high magnetic fields up to 12 T could be performed. Later, experiments down to \( T \approx 1.3 \) K have become possible by mounting the sample holder into a Janis Research SVT-200 variable temperature insert (VTI). This flexibility was achieved by using a leak tight sliding seal (not shown) fitted to the stainless steel tube (I) together with the proper fitting to the actual cryostat or transport vessel. Typically, the measurements were carried out in cryogenic vacuum with the cap (IV) providing leak tight enclosure with indium sealing.

The exploded view of the room temperature part of the assembly is shown in Fig. 3.1b. Here, the stepper motor (1) reclining against its base plate (2) is connected to the axle (4) via a torque limiter coupling (3) which prevents any damage of the sample holder in case the axle gets stuck. The axle goes through the vacuum feedthrough (5) into the vacuum chamber (7). The chamber is sealed with several plastic O-rings at the vacuum feedthrough, the plate (6), and the electronic connection feedthroughs (8) for measurement signals, piezo control and thermometry.

The top plate (10) of the low temperature chamber (Fig. 3.1c) is soldered to the four stainless steel tubes (not shown for clarity here). The indium wire for vacuum sealing is put in the slot of this plate, whereas the vacuum coating (IV) touches with a flat surface and is attached via 12 pieces of M2.5×12 screws. In order to make the sample holder head (12) detachable, a connector assembly (11) was introduced. Two pieces of 6-pin mini-DIN receptors with gold plating were fitted in this part with the mating connectors sitting in the sample holder head. The bottom part of the axle (9) is also a distinct part which connects to the rest of the axle with a U-shaped joint providing the mechanical transmission when rotating the axle. For clarity, it is shown outside of the sample chamber.
Figure 3.1: The design of the sample holder. The outline of the entire assembly (a). The exploded view of the room temperature parts (b) and the low temperature parts (c).
With this design, several tasks, e.g. mounting the sample, can be performed without moving the entire sample holder assembly. This was especially convenient for tasks performed with the aid of optical microscope. Due to the complexity of the sample holder head (12), its detailed assembly is discussed in detail below. The approximate position of the sample and tip is schematically shown in Fig. 3.1a and c. The 1300 mm separation from the room temperature parts is defined by the position of the superconducting magnet in the Oxford Instruments cryostat.

### 3.1.2 The twofold actuation scheme

The sketch of the sample holder head together with a photo is shown in Fig. 3.2. Here, the tip and the sample are denoted by 12d. The separation between them is typically in the 100 µm range prior to cooling down, from which distance the tip will approach the sample and a metallic point contact is formed. In order to accurately tune the junction diameter afterwards, the electrode movement has to be controlled with a precision in the range of the single-atom level.

![Figure 3.2](image)

Figure 3.2: The detailed assembly of the low temperature parts. The cone (a), and the sample holder head (b) and (c).
3.1. MECHANICAL DESIGN

Movements in such a broad range are typically achieved using a twofold actuation scheme whose realization in this sample holder is presented as follows. The coarse actuation is made solely mechanically, using the stepper motor rotating the axle. The axle couples through a fork-blade mechanism to the conical part shown in Fig. 3.2a. On the right hand side of this part (9c) a screw thread M8×0.5 is cut (9c), which fits into the corresponding inner thread (12f) of the sample holder head. In contrast, left hand side of the axle (9a) is merely of cylindrical shape and is a cylinder which can move freely along the axis in the corresponding socket of the sample holder (12a) of the sample holder. The screw thread converts the rotating motion denoted by green arrows to a linear one (blue arrows). As the cone moves, the tip assembly (12c) fixed on the end of a phosphor bronze bending beam (12b) is pressed towards the sample (red arrows). A notable feature of this design is that the conical shape itself acts as a mechanical attenuation between the horizontal movement (blue arrow) and the vertical movement (red arrow) pushing the tip. Here, the attenuation is 1 : 12.5 which allows a maximum tip displacement of 2 mm considering the 25 mm length of the cone.

The resolution of the coarse actuation can be estimated as follows. The resolution of the stepper motor is 4000 steps per revolution (using the microstep capability of the controller electronics), hence the horizontal movement is 0.5 mm/4000 = 0.125 μm. This corresponds to a 0.125 μm/12.5 = 0.01 μm displacement of the tip for a single step of the motor. This ideal resolution is reduced by several practical factors, like the surface roughness of the cone, the sticking of the parts, or the twisting of the long axle. Together with these limiting factors the resolution of the mechanical actuation is still in the sub-micron range.

The fine tuning of the junction geometry is performed by a Microtritor piezo translation stage (12e) manufactured by Piezosystem Jena which is capable of a maximum expansion of 9 μm for the maximal bias voltage of 150 V at room temperature. This value decreases to ~ 1 μm at T = 4.2 K, still providing a reasonable overlap with the sub-micron resolution of the mechanical positioning. The resolution of the piezo actuation is mainly limited by the voltage noise on the actuator. The typical voltage noise of the high voltage power supply is 0.3 mVrms, which is further reduced by a π-filter with a cutoff frequency of 7200 Hz (Fig. 3.3). This noise level corresponds to a picometer scale uncertainty of the piezo displacement, obviously well below the mechanical stability of the setup.

![Figure 3.3](image_url): The schematics of the piezo power supply featuring a π-filter with a cutoff frequency of about 7200 Hz.
3.2 Preparation of the heterojunctions

3.2.1 Sample preparation

While typically thin film samples deposited on a Si substrate were investigated, bulk materials up to a thickness of $\sim 3\text{ mm}$ could fit on the top plate of the piezo. In order to ensure electronic isolation, the samples were mounted on a Kapton foil and glued with a CMR GE Varnish glue. Depending on the sample, either silver paint or indium soldering was used to make the electrical connection on the sample.

3.2.2 Tip preparation

Andreev reflection measurements were mostly performed using Nb tip due to its rigidity and endurance. Nb tips were made from a 1.0 mm diameter wire of 99.9% purity purchased from Mateck GmbH. A sharp tip apex was cut using a sharp scissor, and then the sample holder was rapidly assembled and pumped in order to minimize surface contamination.

Such tips were characterized by making Andreev reflection measurements on a bulk Au sample. In Fig. 3.4, it is shown that the agreement between measurement data taken on different junctions, and the fits based on the BTK theory is excellent. Moreover, the fitted superconducting gap is in good agreement with the bulk $\Delta = 1.55\text{ meV}$ value of Nb.

![Figure 3.4: Experimental data taken on Au-Nb junctions for three different junctions. Solid lines are the fitted curves according to the BTK theory. The parameters of the fits are shown as well.](image-url)

For some characterization measurements when superconductivity was not required, other tip materials, such as tungsten, and Pt/Ir were used as well. Depending on the rigidity of the material, the sharp tip apex was created either by cutting the wire or by using electrochemical etching. It should be noted, that while the mechanical stability of small diameter junctions was rather insensitive to the details of the tip preparation,
3.3. ELECTRONICS

Generally clean conditions and no mechanical impact on the tip after creating the apex was necessary to get proper results. As an example, a suitably sharp tungsten tip is shown in the optical microscope image in Fig. 3.5.

![An optical microscope image of a W tip created by electrochemical etching.](image)

3.3 Electronics

In this section, the measurement electronics utilized to perform the experiments is presented. Generally, the main design consideration was to achieve low noise levels for Andreev reflection measurements. Here it should be emphasized that even if quasi DC measurements are performed, any high frequency noise coming from e. g. microwave radiation, radio signal, thermal noise of room temperature resistors, reaching the sample would smear the nonlinearities of the $I-V$ curves appearing in the mV bias range. Some of the measurements have also required high speed operation involving short bias voltage pulses, demanding a different electronic setup than the low-noise Andreev reflection measurements. The discussion below will go from the simplest measurements merely involving the acquisition of $I-V$ curves, to the high-speed setup and finally to the simultaneous measurement of bias pulses and $I-V$ curves for Andreev reflection experiments.

3.3.1 $I-V$ measurements for Andreev reflection

The setup for the Andreev reflection measurements is show in Fig. 3.6. The junction is voltage biased by the output of the data acquisition card. In these measurements, a National Instruments PCI-6281 card (DAQMX) was used featuring 18 bit and 16 bit resolution for analog input and analog output, respectively. Additionally, digital
I/O and counter inputs are available for auxiliary measurement control. The maximal sample rate of 625 kS/s perfectly suits the needs of the $I - V$ curve measurements.

As the output voltage range of the DAQMX card is $\pm 10$ V a 1 : 100 divider was employed to reduce noise level for measurements performed typically in the 10 mV range. Furthermore an additional $\pi$-filter was added to cut high-frequency noise. Note that the same $\pi$-filter was added to the other line ensuring symmetrical source impedance at the connections of the sample holder. The wiring connecting the room temperature and low temperature parts consists of a commercially available twisted pair cable which itself acts as a low pass filter as well, and highly reduces pickup noise compared to untwisted wiring.

An additional filtering was applied at the low temperature stage. First, a twisted pair cable was made of a $\varnothing 0.05$ mm insulated copper wire of $\sim 100$ cm in length. Then, it was reeled to form a single layer coil on a $\varnothing 2.5$ mm uninsulated copper wire which was brought to good electrical and thermal contact with the sample holder head. The assembly was then coated by copper granulate using an EMV Lack (Cramolin Art.Nr.124) creating a highly conductive covering on the wires. After drying, each line of the twisted pair exhibited $\approx 420$ pF capacitance to the ground making this filter effective for frequencies above $\sim 1$ MHz. The linear coil structure reduces cross-capacitance between the two ends of the wire, hence enhancing filtering in the microwave regime. Furthermore, by ensuring good coupling to the sample holder head, thermalization of the wiring is also ensured.

The current flowing through the junction is measured by a commercially available variable gain I-V converter DLPCA-200, manufactured by Femto GmbH. For Andreev reflection measurements, typically a gain of $10^6$ V/A was used. The output voltage of the I-V converter is sampled by the DAQMX card and read by the measurement program. Typical waveforms during these measurements are illustrated by Fig. 3.7.
3.3. ELECTRONICS

3.3.2 Electronic noise level

Andreev reflection measurements rely on the nonlinearities of the $I - V$ curves on the voltage scale of the superconducting gap, hence the changes of the differential conductance have to be resolved on this scale. This demands a voltage noise level $e\delta V \ll \Delta$ to acquire reliable data.

![Figure 3.7](image1.png)

Figure 3.7: (a) Typical waveforms of the bias voltage drive and the measured current for Andreev reflection measurements. (b) The recovered $I - V$ curve. Red dash lines show the linear slope above the superconducting gap.

![Figure 3.8](image2.png)

Figure 3.8: Typical differential conductance curve recorded on a Pb-Pb tunnel junction with a normal state resistance of $\approx 780 \, k\Omega$. The FWHM of 250 $\mu$V of the peak at the gap edge is shown. The zero bias peak is a small correction due to higher order Andreev reflections.

The typical noise level can be characterized by measuring the $dI/dV$ curves of superconductor – insulator – superconductor (SIS) junctions. Here, narrow peaks appear at $eV = \pm 2\Delta$, whose full width at half maximum (FWHM) characterizes the voltage...
smearing, i.e. the pickup noise present on the junction. Typical experimental data on a Pb-Pb tunnel junction with $2\Delta = 2.55 \text{ meV}$ is shown in Fig. 3.8.

The observed smearing of $\approx 250 \mu\text{V}$ is suitable for measurements using superconductors with relatively large gap, such as Nb or Pb.

### 3.3.3 Mechanical stability

![Feedback Circuit Diagram](image)

**Figure 3.9:** The schematics of the feedback circuit used for testing the mechanical stability of the measurement setup. Note that the details of circuitry inside the sample holder is not shown for clarity.

It is instructive to characterize the sample holder design for mechanical stability, i.e. the capability of holding a junction with a certain resistance stable. This was investigated with the feedback circuitry shown in Fig. 3.9. Here, the junction is biased with a constant 100 mV, and the TS-530 (Picowatt) analog PID circuit regulates for a constant current, by controlling the piezo power supply. A limiter circuit is added to match the wider output range of the PID controller to the input of the power supply. As the cutoff frequency of the PID is $\approx 10 \text{ Hz}$, faster oscillations of the junction conductance can be evaluated for pinpointing typical mechanical noise sources and investigating the inherent stability of the setup. The noise spectra of the current was recorded using an SR770 network analyzer.

A typical spectrum is shown in Fig.3.10a for an Au-Au junction with a setpoint resistance of 20 MΩ. The two broad peaks around 17 Hz and 32 Hz demonstrate that low frequency mechanical noise is the main factor that compromises the stability of the junctions in the tunneling regime. We note that higher frequency contributions up to 100 kHz were found to be negligible. It is important to note, that this data set was recorded ensuring that there is no surface oxide layer between the electrodes that could mechanically support the junction. This is in contrast to e.g. the previous data set for Pb-Pb tunnel junction, where high mechanical stability is attributed to such mechanical support.
3.3. ELECTRONICS

Figure 3.10: (a) The spectral noise density of the feedback signal of an Au-Au junction in the tunneling regime. (b) The ratio of the integrated noise density and the setpoint value as a function of the setpoint resistance. Black dash line denotes the resistance corresponding to a single atomic contact. Red dash line shows the limit of unity.

To further study the mechanical stability of the system, several measurements were made with different setpoint resistances down to 1 kΩ when the gold already forms an ohmic point contact. The ratio of the integrated noise density and the setpoint value is shown in Fig. 3.10b. Here, a drop of approximately two orders of magnitude is visible when the junction is in the point contact regime. The plot also demonstrates that in the tunneling regime the setpoint is actually comparable to the variation, i.e. the integrated noise level, hence the sample holder cannot be used in the vacuum tunneling regime, for which further developments are necessary.

3.3.4 Pulsed measurements

For some experiments, it was necessary to apply short voltage bias pulses on the junction, and to measure the linear resistance in between. Such pulse train is illustrated in Fig. 3.11. The voltage pulses with an increasing amplitude \( V_{\text{pulse}}(i) \) are generated, and the resistance is measured with a bias of \( V_{\text{sense}} \ll V_{\text{pulse}} \) in between. Typically, \( t_{\text{sense}} \gg t_{\text{pulse}} \) is a favorable condition, if the sensing circuitry has smaller bandwidth, or if the Joule heating of the high bias pulse has to be considered.

It is important to note, however, that such mapping is not equivalent to measuring the \( I-V \) curve by a linearly ramped bias voltage. In fact, the full \( I-V \) curve can only be recovered if the current is monitored during bias pulse as well which is limited by the cutoff frequency of the I-V converter. Due to this limitation, two distinct measurement circuit was developed for such experiments. The first one is essentially based on the I-V curve circuit already having \( \gtrsim 500 \text{ kHz} \) bandwidth if the \( \pi \)-filters are removed. For faster operation, however, a separate arbitrary waveform generator had to be employed making pulse widths down to the 10 ns range possible. A drawback of this circuitry is
3.3. ELECTRONICS

that the full $I - V$ curve cannot be recovered anymore, only the zero bias resistance is measured.

**Pulsed measurements using the DAQMX card**

The schematics of the measurement setup is shown in Fig. 3.12. Since typically $V_{\text{sense}} = 100$ mV and $V_{\text{pulse}} = 100$ mV ... 1 V were used, the 1 : 100 divider and room temperature filtering were removed. The bandwidth of this circuit is limited by the 500 kHz cutoff frequency of the I-V converter, and the 625 kS/s sampling rate of the DAQMX card. Despite these limitations, the entire waveform shown in Fig. 3.11 could be conveniently output by the DAQMX card and the response could be recorded as well. It should be noted that while the sampling rate of the DAQMX card allowed for $t_{\text{pulse}} \geq 1.6 \mu s$, the full $I - V$ curve could be recorded for $t_{\text{pulse}} \gtrsim 5 \mu s$ limited by the bandwidth of the I-V converter.

![Figure 3.11: The timing diagram of pulsed measurements.](image)

Figure 3.11: *The timing diagram of pulsed measurements.*

![Figure 3.12: The schematics of the setup for applying bias pulses using solely the DAQMX card.](image)

Figure 3.12: *The schematics of the setup for applying bias pulses using solely the DAQMX card.*
3.3. ELECTRONICS

Pulsed measurements using arbitrary waveform generator

For narrower pulse widths an Agilent 81150A external waveform generator was used capable of producing $t_{\text{pulse}}$ values in the 1 ns range. In order to reduce smearing of such short pulses, the low temperature filtering, and the twisted pair cable had to be removed from the signal path and replaced by a coaxial cable as shown in Fig. 3.13. For this circuit, the waveform presented in Fig. 3.11 is programmed into the 81150A unit. During the duration of the pulse, the relay is in its upper position, so that the I-V converter is excluded from the signal path. After the pulse, however, the relay switches, and the current flows through the I-V converter so that the linear resistance can be measured. The limitation of this circuit is that the sample itself is not matched to the 50Ω impedance of the rest of the circuit. Nevertheless, by evaluating the shape of the waveform using a Lecroy 500 MHz digital sampling oscilloscope, rise and fall times better than 20 ns were found for junction resistances in the 100 Ω range.

![Figure 3.13: The schematics of the setup for applying voltage pulses using an external waveform generator.](image)

3.3.5 Simultaneous Andreev reflection and pulsed measurements

The recording of the full $I-V$ curve necessary for Andreev reflection measurements together with the capability of applying narrow pulses on the junction needed a more complex circuit shown in Fig. 3.14 which can be regarded as the modified version of Fig. 3.6. By introducing the relay boxes, the divider box, the $\pi$-filters and the I-V converter can be removed from the signal path, hence making high speed operation possible similarly to Fig. 3.12. This operation is demonstrated by the red pulses in Fig. 3.15. Then, by reversing the relays, we get the same circuit as in Fig. 3.6, making low noise Andreev reflection measurements possible. In this setup, the linear bias ramp maps the $I-V$ characteristics, and differential conductance curves are recovered by numerical differentiation. Typically, a ramp amplitude in the mV regime was used, in contrast to the pulse amplitude being the order of 1 V.
The simultaneous control of the relays and the analog circuitry especially demanded a highly automated measurement control software which will be briefly introduced in the next section. In order to prove that no additional noise was introduced due to the more complex design, Andreev reflection measurements on SN junctions have been performed and shown no sign of additional smearing at $T = 4.2 \text{ K}$. A notable limitation of this setup is that the minimum bias pulse width is in $\mu\text{s}$ range, as the low-noise Andreev reflection measurements demand the presence of the noise filtering hindering pulsed measurements in the ns time scale.
3.4 Computer control

The real-time control of the point contact geometry and the high volume data acquisition for the $I-V$ curve measurements demands a highly automated measurement control system. The control program running on the host computer was developed in Microsoft Basic.NET object-oriented programming language using the Visual Studio IDE. In order to suit this general purpose programming environment to the needs of this project, the Measurement Studio software package developed by National Instruments was employed. This software introduces additional classes vital for real-time visualization of measurement data, or for communication with scientific instruments.

The goal was to design a software that provides convenient control of the measurement, while the acquired data is visualized on the fly so that the experiments can be repeated in the same run if necessary. The key features can be summed up in the following points:

- **Automatic control of the tip approach.** In the beginning of the measurement, the spacing between the tip and the sample is typically in the $100\,\mu$m regime. This is reduced by slowly turning the axle using the stepper motor, while the piezo actuator is fully elongated. As soon as a tunnel current $\sim 1\,\text{nA}$ is detected, the stepper motor is stopped and the piezo retracts for further protection of the tip and the sample. This control was developed by employing the sophisticated triggering capabilities of the DAQMX measurement hardware.

- **Continuous control of the junction size throughout the measurement.** With the software control of the piezo power supply, the slow drifting of the junction can be eliminated by using a feedback loop of the point contact resistance. This prevents the junction from collapsing, i.e. going to very low resistances that can cause an irreversible change of the tip shape affecting the mechanical stability.

- **Automated acquisition of the $I-V$ curves.** The desired amplitude and sweep rate can be set via the user interface, and data collection is performed automatically afterwards. Moreover, in addition to the triangle waveform used for Andreev reflection measurements, arbitrary waveforms can be programmed for e.g. voltage pulse experiments.

The user interface of the measurement control software is shown in Fig. 3.16. The piezo control is found in the upper left corner, being in manual mode in this screenshot. The junction resistance as a function of the time is visible below the piezo control, while the acquired $I-V$ curve (green line) is on the right. Here, additional linear fits (blue and red lines) are shown for evaluating the linear slope and the excess current of the measurement data. Further control parameters are displayed and can be set with the controls above the graphs.
Figure 3.16: The user interface of the measurement control software.
Chapter 4

Spin polarization and coherent diffusive effects

In this chapter, point contact Andreev reflection measurements are shown for the (In,Mn)Sb and (In,Be)Sb compounds. (In,Mn)Sb is a dilute magnetic semiconductor (DMS), which has been thoroughly characterized by earlier magnetotransport and structural characterization measurements [59,131]. (In,Be)Sb is the nonmagnetic counterpart of (In,Mn)Sb serving as a reference material, where spin polarization is not expected to be found.

First these materials are investigated to check the reliability of spin polarization measurements based on Andreev spectroscopy. It is found that the creation of small, ballistic contacts is essential for reliable spin polarization measurements. In diffusive junctions a considerable smearing of the differential conductance curve is found, and additionally a zero bias peak (ZBP) is observed for the (In,Be)Sb sample, both hindering the accurate determination of the spin-polarization.

Further investigating the ZBP phenomenon for the (In,Be)Sb sample, we demonstrate the role of finite voltage bias and temperature eventually suppressing the ZBP. Finally, we demonstrate the formation of proximity superconductivity beneath the junction, as reflected by the emergence of the Josephson current at zero bias.

4.1 Sample details

We briefly summarize the growth and characterization of the samples [59,132]. The samples were grown by the group of Prof. J. K. Furdy na at the Department of Physics, University of Notre Dame. The substrates were prepared by Prof. T. Wojtowicz, at the Institute of Physics of the Polish Academy of Sciences. The electronic transport and structural characterization was performed at the University of Notre Dame, prior to our Andreev reflection studies.

The (In,Mn)Sb and (In,Be)Sb films with typical thicknesses of 230 nm were grown by molecular beam epitaxy in a Riber 32 R&D system. During growth, in situ reflection high energy electron diffraction (RHEED) characterization was performed, whereas
4.2. ACCURACY OF THE SPIN POLARIZATION MEASUREMENTS

Further structural characterization was done by X-ray diffraction afterwards. The distribution of the Mn atoms inside the host lattice was evaluated by Rutherford backscattering (RBS) and particle-induced X-ray emission (PIXE) indicating that ≈ 85% of the dopants occupy substitutional positions in the III-V host lattice contributing to the ferromagnetic ordering.

The hole concentration of the (In,Mn)Sb sample is \( n = 2 \times 10^{20} \text{ cm}^{-3} \), as determined by earlier Hall effect experiments [59]. The resulting metallic resistivity of \( \rho \approx 400 \mu\Omega \text{cm} \) is dominated by the temperature independent residual resistivity. The estimated mean free path based on the band parameters of the InSb compound [133] is \( l_m \approx 15 \text{ nm} \).

Similarly, for the (In,Be)Sb sample \( n = 1.4 \times 10^{20} \text{ cm}^{-3} \) and \( l_m \approx 9 \text{ nm} \) was found.

4.2 Accuracy of the spin polarization measurements

The Andreev reflection measurements were performed at 4.2 K using a mechanically sharpened Nb tip. The statistical characterization was performed by studying several contacts at different lateral positions of the sample.

4.2.1 Ballistic point contacts

Demonstrative differential conductance curves together with the fits based on the modified BTK theory are shown in Fig. 4.1. Our dataset confirms the ferromagnetic ordering in the (In,Mn)Sb sample, exhibiting a charge carrier spin polarization of \( P_c = 0.60 \). For the nonmagnetic (In,Be)Sb \( P_c = 0.03 \) was obtained. The normal state resistances for these specific junctions were \( R_N = 714 \Omega \) and \( R_N = 2362 \Omega \) for the (In,Mn)Sb and the (In,Be)Sb sample, respectively. Based on the Wexler equation (2.9), the estimated junction diameters of 11 nm and 8.5 nm are both below \( l_m \) indicating ballistic transport which is an essential requirement of the BTK theory.

While the modified BTK theory gives a reasonable fit for the measurement data, the error of the extracted spin polarization value should carefully be estimated. This can be done by checking how the curves can be fitted at a purposely detuned, constant \( P'_c = P_c \pm \delta P_c \) value, using only the barrier strength \( Z \) as a fitting parameter. Such fits are shown in Fig. 4.2a. It is apparent, that a change of 0.1 in \( P_c \) already renders the fit quite poor, therefore \( P_c \) can be fitted with an accuracy much better than \( \Delta P_c = 0.1 \) in the high junction transparency limit. This proves that Andreev reflection spectroscopy is an appropriate method for determining the spin polarization in ferromagnetic materials.

In order to further support the analysis of the spin polarized transport on the basis of our measurements, the two evaluation models discussed in Section 2.4.2 were compared (Fig. 4.2b). The modified BTK model results in \( P_c = 0.60 \) and \( Z = 0.13 \) (black line plot). The barrier strength corresponds to a \( T = (1 + Z^2)^{-1} = 0.98 \) indicating that the junction has high transmission which is vital for reliable analysis. The alternative analysis based on the spin-dependent transmission eigenvalues gives \( T_\uparrow = 0.99 \) and \( T_\downarrow = 0.246 \) resulting in a spin polarization of \( P_H = 0.605 \) according
4.2. ACCURACY OF THE SPIN POLARIZATION MEASUREMENTS

Figure 4.1: Andreev reflection spectra for (In,Mn)Sb (a) and for (In,Be)Sb (b) exhibiting a spin polarization of $P_c = 0.60$ and $P_c = 0.03$, respectively. Solid lines show the fitted curves according to the modified BTK theory.

Figure 4.2: The reliability of the recovered spin polarization, as demonstrated on actual experimental data for (In,Mn)Sb. (a) Red solid line: the best fit resulting in $P_c = 0.60$. Blue and green dash lines: Best fits with the detuned $P'_c$ values shown for each curve. (b) Comparison of the modified BTK model (black line) and the Hamiltonian transport model (red curve). The deviation is shown in the bottom (green line) compared to the scattering of the experimental data (blue line).

to (2.66) which is in excellent agreement with the value recovered using the modified BTK model. The $T_\uparrow$ transmission is close to the transmission $T$ of the modified BTK model. It should be stressed, however, that $T_\uparrow$ and $T_\downarrow$ cannot be directly mapped to the single $T$ value.
4.2. ACCURACY OF THE SPIN POLARIZATION MEASUREMENTS

4.2.2 Ballistic-diffusive crossover

To study the size dependence of Andreev reflection measurements several point contacts have been investigated over a wide interval of the junction sizes, ranging from the ballistic to the diffusive limit. The junction diameters have been estimated to be in the range of \( d = 5 \text{ nm} \ldots 50 \text{ nm} \) based on the Wexler equation (2.9).

\[
\frac{\Gamma}{\Delta} = \frac{1}{d} \quad \text{for } d \leq 15 \text{ nm}
\]

Figure 4.3: (a) The size dependence of the Andreev spectra. Differential conductance curves for junctions in the ballistic limit (down) and in the diffusive limit (top) for (In,Be)Sb and (In,Mn)Sb together with the corresponding fits plotted as solid lines. Note that the ZBP is excluded from the fits for the (In,Be)Sb sample. (b) The recovered quasiparticle broadening (\( \Gamma \)) as a function of the contact diameter \( d \). Red circles and black squares denote data acquired on (In,Mn)Sb and (In,Be)Sb samples, respectively. An upturn is visible for \( d \gtrsim 15 \text{ nm} \). The dash line is a guide to the eye.

Compared to the previously analysed ballistic junctions, an emerging broadening is observed of the differential conductance curves. Due to this broadening, the curves can only be fitted by using either an elevated temperature value, or a quasiparticle broadening parameter, \( \Gamma \). In the first case, the fitted temperatures can even be higher than the superconducting critical temperature of the Nb tip, at the same time with a well developed superconducting gap. This is obviously unphysical, therefore the phenomenological broadening parameter \( \Gamma \) was used in the fits.

Fig. 4.3b shows a systematic investigation of \( \Gamma \) for a wide variety of junctions. It was found to be reasonably small for junctions with small diameters, whereas it rapidly increases for \( d > 15 \text{ nm} \) (Fig. 4.3b). This threshold value is in good agreement with the estimated mean free path in the DMS compound, hence the smearing is related to the diffusive transport and attributed to the enhanced scatterings in the junction area in the diffusive regime.

The presence of a significant broadening parameter obviously spoils the accuracy of the obtained spin polarization, therefore it is essential to use ballistic junctions for Andreev spectroscopy measurements.
Beside the broadening of the differential conductance curve the appearance of a zero bias peak was also observed (Fig. 4.3a), which was exclusive for (In,Be)Sb contacts. This zero bias peak is also clearly related to the diffusive nature of the transport, as discussed in the following section.

4.3  Coherent diffusive effects

In Section 2.3.2, it was demonstrated that in diffusive SN junctions different quantum interference effects may occur that result in a correction of the conductance. The zero bias peaks in the differential conductance of (In,Be)Sb samples (Fig. 4.3a) very much resemble the reflectionless tunneling phenomenon which manifests itself as a zero bias peak (ZBP) in the conductance. In the following we analyse this additional structure in detail to study the nature of mesoscopic proximity effect in SN junctions.

First we note that ZBP was only observed for the (In,Be)Sb samples, similar features were never seen in (In,Mn)Sb. This difference is clearly related to the magnetic ordering of (In,Mn)Sb: the considerably exchange splitting leads to rapid dephasing of the charge carriers in the diffusive volume.

4.3.1  Junction size and temperature dependence

Fig. 4.4 shows demonstrative differential curves of the (In,Be)Sb sample at different contact diameters demonstrating the gradual increase of the zero bias peak as the contact diameter ranges from the ballistic regime (bottom curve) to the diffusive regime (top curve).

Figure 4.4: Differential conductance curves for (In,Be)Sb-Nb junctions at $T = 4.2K$. The normal state resistances are shown for each plot, respectively. The curves are shifted for clarity.

Typical differential conductance curves are shown in the ballistic (bottom) and the diffusive regime (up) in Fig. 4.4. The transmission of the junctions can be then eval-
uated in the ballistic regime using the BTK theory. By analyzing $\approx 10$ distinct point contact, an average $Z = 3.0 \pm 0.5$ is obtained which corresponds to a transmission of $T_S = (1 + Z^2)^{-1} \approx 0.1$. For diffusive junctions the barrier strength cannot be determined accurately, therefore one can only assume that the transmission is similar to that of ballistic junctions. The $T_S \approx 0.1$ transmission corresponds to the low transmission regime, therefore the interpretation of the positive zero bias peak by reflectionless tunneling phenomenon is justified.

![Figure 4.5: The $I-V$ (a) and the differential conductance (b) curves of junctions with $R_N = 400 \Omega$ at different temperatures.](image)

In order to investigate the temperature dependence of the amplitude of the ZBP, a series of measurements were performed at different temperatures for a normal state resistance $R_N = 400 \Omega$. Based on the Wexler equation [42,43] this resistance corresponds to a junction diameter of $r \approx 200 \text{nm}$. This contact size is well above $l_m$, thus the junction is in the diffusive regime. Typical $I-V$ and differential conductance curves are shown in Fig. 4.5 at different temperatures.

It is found, that the zero bias peak only appears for $T \lesssim 3.5 \text{K}$. This is well below the superconducting transition temperature. At such low temperatures no substantial variation of the superconducting ordering is expected, therefore the temperature dependence of the ZBP cannot be related to the variation of the superconducting gap. This suggests the presence of another temperature scale.

Further increasing the junction diameter, a very sharp ZBP is found in the low temperature limit rather resembling a Josephson current characteristic to superconductor – insulator – superconductor junctions (Fig. 4.6) instead of the reflectionless tunneling phenomenon.
4.3. COHERENT DIFFUSIVE EFFECTS

![Graph showing I-V and differential conductance curves](image)

Figure 4.6: The $I-V$ (a) and the differential conductance (b) curves of junctions with $R_N = 100\, \Omega$ at different temperatures. Note the fourfold change in the conductance scale above the dash line.

4.3.2 Statistical analysis of the ZBP properties

In order to gain insight to the details of this apparent transition, numerous measurements were performed at different temperatures and junction area sizes. Comparing Fig. 4.5 and Fig. 4.6, a possible parameter to investigate is the width of the ZBP on the bias voltage axis. This width is plotted in Fig. 4.7 as the function of the normal state resistance of the junction. Temperature values ranging from 1.6 K to 4.2 K are denoted by different colours.

![Graph showing ZBP width vs. normal state resistance](image)

Figure 4.7: The evolution of the width of the ZBP with the junction resistance at different temperatures. Dashed regions are discussed in the text.

In the low temperature limit, the peak width apparently shrinks below a certain resistance resistance range denoted by the dash region in Fig. 4.7. The corresponding
Figure 4.8: Evolution of the zero bias peak with increasing contact size at $T = 1.6\, K$. Dash line indicates the upper theoretical limit for the peak amplitude in SN junctions, $G_{\text{max}}(V = 0) = 2G_{\text{normal}}$. The differential conductance curves are normalized to the normal state resistances of the contacts, which are: (a) 994 $\Omega$, (b) 250 $\Omega$, (c) 130 $\Omega$, respectively.

The junction radius is $r^* = 250\, \text{nm} \ldots 650\, \text{nm}$ as estimated from the Wexler equation. We note that the uncertainty of $r^*$ is determined by the error of the barrier strength $Z$. For junction resistances above the transition region (right hand side of Fig. 4.7), the width is found to be in the same order of magnitude with the energy scale of the temperature range of our measurements ($140\, \mu\text{eV} \ldots 360\, \mu\text{eV}$, see the dotted lines in Fig. 4.7). It should be noted, however, that due to the excessive junction to junction variation, no systematic temperature dependence could be recovered. For larger area junctions (smaller resistance, the left hand side of Fig. 4.7), however a transition temperature of $T^* \sim 2.5\, K \ldots 3.0\, K$ is present, below which the width of the ZBP appears to shrink one order of magnitude.

The presence of this transition is further emphasized by comparing the amplitude of the ZBP to the maximum value $G(V = 0) = 2G_N$ for SN junctions [134, 135]. In the low temperature limit, $T = 1.6\, K$, for large junctions, this limit is lifted, and an almost tenfold increase is found in the conductance (Fig. 4.8). The $G(V = 0)/2G_N$ ratio as a function of the normal state resistance and the temperature is systematically investigated in Fig. 4.9. Similarly to Fig. 4.7, a clear transition is observed: at low enough temperatures and large enough contact sizes the amplitude of the ZBP exceeds the limit for SN junctions (denoted by dash line in Fig. 4.9). Furthermore, the transition temperature $T^*$ and junction radius $r^*$ are the same as those in Fig. 4.7.

Discussing the experimental observations, first we emphasize that both the width and the amplitude of the zero-bias peak indicate a rather sharp transition at a critical temperature and critical contact radius. For small contacts and high temperatures zero-bias peaks with finite width and moderate amplitudes are observed, which are attributed to reflectionless tunneling phenomenon. However, for $T < T^*$ and $r > r^*$ the width of the peak abruptly decreases and its height grows highly above the theoretical upper limit for SN junctions.
4.3. COHERENT DIFFUSIVE EFFECTS

Figure 4.9: Two-dimensional plot of the ratio of the zero-bias conductance and the normal state conductance as the function of the point-contact resistance and the temperature. Measured data points are indicated by black dots. The threshold value of 2 is indicated by a dash line. The three characteristic regions denoted by (a), (b) and (c) are discussed in the text.

Such a narrow peak, resembling to the critical current in superconductor – insulator – superconductor junctions [136], however, can be addressed by taking proximity induced critical current into account. That is, for reasonably strong coupling, a Josephson current can flow between a superconductor (S), and the proximity-induced superconductor (S’) region [137, 138]. It should be noted, that this proximity induced critical current is not an exactly zero bias feature, instead a finite width ZBP is found in the differential conductance. Nevertheless, this peak is much narrower than the broadening $k_B T$ defined by the temperature, clearly separating this feature from reflectionless tunneling as well [139]. Furthermore, the increase of the zero bias conductance $G(V = 0)$ with respect to the normal state conductance $G_N$ clearly exceeds the limit of ($G(V = 0) = 2G_N$) for SN junctions further stressing the role of the superconducting pair correlations in the normal lead.

4.3.3 Discussion

First we discuss the preconditions for the appearance of the ZBP in the reflectionless tunneling regime. Within the framework of the two-barrier model of the diffusive junctions (see Section 2.3.2 for details), this feature is expected if the transmission of the two barriers are in the same range, $T_N \sim T_S$. In the (In,Be)Sb sample, the mean free path is $l_m \approx 9 \text{ nm}$ and the layer thickness $L = 230 \text{ nm}$ beneath the junction, so the average transmission of the diffusive volume can be estimated based on the random matrix theory [80]:

$$\langle T_N \rangle \sim \frac{l_m}{L} \approx 0.04.$$ (4.1)
4.4. CONCLUSIONS

The transmission of the SN interface was estimated based on BTK fits for ballistic junctions, and was found to be $T_S \approx 0.1$. Even though both $\langle T_N \rangle$ and $T_S$ are estimated values, merely providing the orders of magnitude, their correspondence verifies the condition $\langle T_N \rangle \sim T_S$ for a reasonably large ZBP.

Turning to the critical current behavior, we first discuss the geometrical constric-
tions present in the system. The size of the volume where coherence is preserved is
defined by the phase coherence length, determined by the temperature at zero bias:

$$L_T = \sqrt{\frac{\hbar D}{k_B T}},$$

(4.2)

where $D = 0.019 \text{m}^2/\text{s}$ is the diffusion constant calculated from the transport prop-
erties of the (In,Be)Sb layer. Substituting the critical temperature of $T^* \approx 2.5 \text{K}$ a phase
cohere length of $L_T^* \approx 250 \text{nm}$ is obtained at the crossover temperature, which coin-
cides with the thickness of the sample. This implies that proximity superconductivity
builds up as the phase-coherent scattering region reaches the bottom surface of the
sample, and the density of the phase-coherent electron-hole pairs is enhanced by sur-
face backscattering. Moreover, the critical contact radius $r^* = 250 \text{nm} \ldots 650 \text{nm}$ shows
good agreement with the thickness of the sample, indicating that the critical cohe-
rent volume for the Cooper pair formation is reached when the radius of the contact
becomes larger then the thickness of the normal region.

Based on these considerations the parameter space of our measurements can be
divided into three characteristic regions. If the contact size is larger than the sample
thickness, then most of the trajectories can bounce back and forth between the SN
junction and the bottom of the sample. If this entire region is phase coherent, i. e. the
trajectories do not lose phase information during several backscattering events, a pro-
ximity superconductivity builds up, and a proximity-induced critical current behavior
is observed [region (a) in Fig. 4.9]. In contrast, only a small number of trajectories are
scattered back coherently if the phase coherent region does not reach the bottom of
the sample. In this case the conventional reflectionless tunneling is observed even for
very large junctions [region (b) in Fig. 4.9]. If the contact radius is smaller than the
thickness of the sample, the normal region can be treated as an infinitely thick elec-
trode, thus no crossover temperature is observed and only a small correction is found
in the zero bias conductance [region (c) in Fig. 4.9].

4.4 Conclusions

It has been successfully demonstrated that point contact Andreev reflection spec-
troscopy is a useful method to determine the charge carrier spin polarization. For the
(In,Mn)Sb sample, on which detailed measurements were performed, $P_c = 0.60$ was
found at $T = 4.2 \text{K}$, where the sample is in the ferromagnetic phase. In comparison,
the nonmagnetic (In,Be)Sb sample of roughly the same dopant concentration, have
exhibited essentially zero spin polarization.
The good quality of the fits has been demonstrated by refitting experimental data with a fixed $P'_c$ which differs from the result of the best fit. It was shown that already a detuning of $\delta P'_c = 0.1$ yields to rather poor fits, hence the error of the fitting procedure is certainly smaller than this value.

By comparing the two theoretical models discussed in Section 2.4.2, a good agreement was found for junctions with high transmission. Specifically, for the (In,Mn)Sb both calculations yield to a spin polarization of 60%, with a deviation smaller than the uncertainties of the fits. It should be noted, however, that for low transparency junctions still exhibiting spin polarized transport, the deviation is typically higher.

A detailed investigation of the influence of the junction diameter on the acquired Andreev spectra has revealed that by creating larger point contacts, the features in the differential conductance curves smears out. This demonstrates the importance of ballistic transport, i.e. small junctions for reliable analysis of the spin polarization.

Further investigations in the diffusive regime on the (In,Be)Sb sample demonstrated the appearance of coherent backscattering, which is observed as a positive correction in the conductance near zero bias. This phenomenon, often referred to as reflectionless tunneling, is characteristic of diffusive superconducting – normal metal junctions in the tunneling regime. By systematically investigating the contribution of the ZBP to the conductance, a transition to a critical current-like behavior is observed as a function of the temperature and the junction diameter. This is attributed to the formation of a proximity superconducting region beneath the point contact, which gives rise to a Josephson current-like behavior.
Chapter 5

The spin diffusion length in metals

The topic of this chapter is the investigation of the decay of the injected spin polarization in nonmagnetic metals. The current perpendicular to the plane (CPP) geometry has been adopted from earlier spin valve experiments (Fig. 5.1a). However, instead of investigating the magnetoresistance of the ferromagnetic (FM) layer – nonmagnetic (NM) spacer – (FM) ferromagnetic layer structure, Andreev reflection spectroscopy was applied to directly measure the decay of the spin polarization in the nonmagnetic layer deposited on the top of a ferromagnetic film (Fig. 5.1b).

First, the detailed parameters of the investigated samples are discussed, then the common experimental considerations are presented. We will separately show our results on Fe/Au and Co/Pt bilayers, respectively. The evaluation of the spin diffusion length will also make it possible to compare our results to that of different measurement methods and conclude on the feasibility of Andreev reflection measurements for deducing the spin diffusion length. Finally, the role of different scattering processes, such as electron-phonon and elastic impurity/boundary scattering are identified in the temperature dependence of the spin diffusion length.

Figure 5.1: The traditional CPP spin valve geometry used to determine the spin relaxation in the NM layer by measuring the amplitude of the magnetoresistance (a). Measurement of the spin relaxation by Andreev reflection, where the spin polarization on the top of the NM layer can directly be extracted (b).
5.1 Experimental details

5.1.1 Sample preparation

The ferromagnet (FM) – nonmagnetic (NM) bilayers were prepared in the KFKI Research Institute for Particle and Nuclear Physics by the group of Dr. F. Tanczikó using molecular beam epitaxy (MBE). First, a thick FM layer was deposited onto a silicon substrate, then the NM layer of different thicknesses was evaporated. The samples of different NM layer thicknesses were produced in a single run, by appropriately shuttering different parts of the Si wafer. We have performed measurements on Co/Pt and Fe/Au FM/NM layers. The detailed parameters for each sample are shown in Table 5.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer</th>
<th>Grow rate (Å/s)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Au</td>
<td>Fe</td>
<td>0.45</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>0.208</td>
<td>5,10,20,40,80</td>
</tr>
<tr>
<td>Co/Pt</td>
<td>Co</td>
<td>0.22</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>0.22</td>
<td>20,40,80</td>
</tr>
</tbody>
</table>

Table 5.1: Layer thicknesses and deposition rates for the bilayer structures investigated.

The NM layer thicknesses included in this work were chosen to be in the range of the spin diffusion length $l_s$ according to earlier results [6] obtained at $T = 4.2$ K. Hence, the variation of the temperature or the layer thickness is expected to have the maximum impact on the results.

5.1.2 The measurement setup

The measurements were performed in cryogenic vacuum in the temperature range of $T = 1.5$ K ... 8.0 K. The experiments were done in a Janis VTI cryostat with a base temperature of $T_{\text{base}} \approx 1.3$ K. The SN contacts were created by pushing a mechanically sharpened Nb tip to the sample. The maximum temperature where the Andreev reflection measurements could be evaluated was found to be $T \approx 8.0$ K. This is determined by the gradual decrease of the superconducting gap of the Nb tip and the increase of the smearing of the electronic distribution function.

Care was taken not to crush the NM surface layer while performing the measurements. This goal was achieved by continuously controlling the diameter of the junction keeping it below $\sim 10$ nm.

5.2 Measurements on the Fe/Au sample

We have performed a detailed investigation of the spin polarization as the function of the Au layer thickness. Moreover, in order to ensure the reliability of the spin polarization fitting procedure, we independently determined the $P_c$ and $P_H$ values
corresponding to the modified BTK theory and the Hamiltonian description of the spin polarized transport. The measurements discussed below were performed at a fixed temperature of 4.2 K.

In order to demonstrate the influence of the Au layer thickness \(d\) on the spin polarization, we present typical differential conductance curves in Fig. 5.2, where the two models of the spin polarized transport are compared by fitting our measurement data. The fitted spin polarization decays with the increasing thickness, as expected.

![Figure 5.2: Measured differential conductance curves for the Fe/Au bilayer sample for different Au layer thicknesses shown for each curve, respectively. (a) The solid lines are fitted curves with the modified BTK theory. (b) The same experimental data are fitted with the Hamiltonian transport approach. The resulting parameters are presented for each curve, respectively. The curves are normalized to their normal state conductance and shifted for clarity.](image)

The modified BTK theory (solid lines in Fig. 5.2a) provides the current spin polarization \(P_c\) and the interfacial barrier strength \(Z\). In contrast, the parameters of the Hamiltonian model addressing spin polarized transport are \(T_{\uparrow}\) and \(T_{\downarrow}\), and the associated spin polarization \(P_H\) is defined by equation (2.66). The fitted transmissions and the derived \(P_H\) values are shown in Fig. 5.2b for each curve.

Generally, a good agreement is found between the associated \(P_c\) and \(P_H\) values even though the two models cannot be mapped onto each other. An excellent agreement is found for the \(Z \to 0\) limit, where the corresponding majority transmission is \(T_\uparrow \lesssim 1\). For higher \(Z\), i.e., lower barrier transmission, typically \(P_c < P_H\) is found with the maximum difference of \(\approx 0.1\). It is also important to note that the relation \(T = (1 + Z^2)^{-1}\) valid for \(P_c = P_H = 0\) cannot be used for the spin polarized case. Instead, \(T_\uparrow \gtrsim (1 + Z^2)^{-1} > T_\downarrow\) holds, further emphasizing the fundamentally different approach of the two models. Nevertheless, the obtained spin polarization values are in good
agreement, their difference is in the range of the fitting procedure’s uncertainty ($\Delta P \approx 0.05$) in the high transmission regime.

The deduced spin polarization values were averaged over about 10 distinct junctions for each Au layer thickness in order to gain a good statistics, and average out possible lateral inhomogeneities of the polycrystalline samples. Then the measurement data were fitted with an exponential decay (Fig. 5.3):

$$P_c(d) = P_0 e^{-\frac{d}{l_s}},$$

where, $l_s$ is the spin diffusion length and $P_0$ is the bulk spin polarization of the underlying FM layer. This assumes that the spin flip scattering on the FM-NM interface is negligible.

![Figure 5.3: The spin polarization as a function of the Au layer thickness, $d$. Solid line shows the fitted exponential decay.](image)

Fitting the exponential decay results in $l_s = (53 \pm 6)$ nm and $P_0 = 0.65 \pm 0.03$. Comparing these values to literature data, we find a good agreement with earlier measurements of the spin diffusion length in the CPP geometry [6, 140]. The $P_0$ spin polarization is, however, significantly higher than the results of earlier Andreev reflection measurements on bare Fe layers $P = 0.42 \ldots 0.45$ [34, 86]. A possible reason for this deviation is the presence of the Au layer acting as a capping layer hence preventing surface degradation in our experiments.

5.3 The spin diffusion length in Pt

5.3.1 Experimental results

Typical differential conductance curves measured on the Co/Pt samples are shown in Fig. 5.4 together with the fits to the modified BTK theory. A typical interfacial barrier strength of $Z \approx 0.5$ corresponds to an average transmission of $T = (1 + Z^2)^{-1} \approx 0.8$, demonstrating the high transparency of the junctions. The gradual decrease of
the fitted spin polarization $P_c$ is demonstrated for a constant Pt layer thickness of $d = 20$ nm with increasing temperature (Fig. 5.4a). The thickness dependence of $P_c$ at a constant $T = 3.5$ K temperature is shown in Fig. 5.4b.

Figure 5.4: Differential conductance curves for the Co/Pt bilayer structure. Solid lines show the fitted curves for the modified BTK theory. The parameters of the fit are shown for each curve, respectively. (a) Results at different temperatures for $d = 20$ nm. (b) Experimental data at $T = 3.5$ K for different Pt layer thicknesses. The curves are shifted for clarity.

In the following, all data points correspond to an average over $\sim 10$ junctions created at different lateral positions on the sample for each temperature value. This procedure made it possible to average out lateral inhomogeneities of the polycrystalline samples.

In order to verify that the systematic decrease of the spin polarization with the increasing temperature is not an artifact caused by the fitting procedure, the barrier strength $Z$ and the superconducting gap $\Delta$ are also shown as a function of the temperature in Fig. 5.5a. No systematic deviation of $Z$ was found from the mean value of $\bar{Z} = 0.54 \pm 0.11$ proving that the variation of the curves with the temperature is not a surface effect. It is important to note that the superconducting gap was also a free fitting parameter. This provides the possibility to compare the resulting values to the BCS superconducting gap (Fig. 5.5b). A good agreement has been found assuring a good quality fit for the spin polarization. For comparison, the energy scale defined by $k_B T$ is also plotted (red dash line) indicating the useful temperature range of the measurements.

The sample dependence of the barrier strength was also investigated in order to exclude surface effects due to sample to sample variation. The average barrier strength $\bar{Z}$ over the entire temperature range is plotted as a function of the $d$ layer thickness in Fig.5.5c. Here, no apparent variation was found, suggesting that measurement data taken on different samples can be compared to deduce the $P_c(d)$ function.
5.3. THE SPIN DIFFUSION LENGTH IN PT

The measured data were compared to the expected variation of the spin polarization:

\[ P_c(T, d) = P_0 e^{-\frac{d}{l_s(T)}} \]  \hspace{1cm} (5.2)

where \( P_0 \) is the bulk spin polarization of the FM layer, and \( l_s \) is the spin diffusion length. The temperature dependence of \( P_c \) is solely attributed to \( l_s(T) \) which is justified at low enough temperatures, i.e. well below the Curie temperature of the FM layer, where \( P_0 \) is regarded as constant. In order to find the relevant sources of spin relaxation, a power law temperature dependence is assumed for \( l_s \):

\[ l_s(T) \propto T^{-\alpha} \]  \hspace{1cm} (5.3)

with the exponent \( \alpha \) being characteristic to the dominant scattering process causing spin relaxation via the spin-orbit coupling [4].

The temperature dependence of the spin polarization for the \( d = 20 \text{nm} \) sample is fitted against (5.3), and \( \alpha = 2.6 \pm 0.8 \) is found (solid and dash line in Fig. 5.6a).

It is important to note that in the low temperature limit, i.e. below \( T \approx 4 \text{K} \), where \( d \ll l_s \), the decay of \( P_c \) becomes exponentially small, thus the temperature dependence of \( l_s \) cannot be extracted. This region is denoted by the dash line in Fig. 5.6a.

Beside the detailed temperature dependence of the 20 nm thick sample (Fig. 5.6a), samples with 40 nm and 80 nm Au layer thickness were also studied at some distinct temperature values. These measurements can be used to plot the \( P_c(d) \) dependence and determine the spin diffusion length from the exponential decay (see inset in Fig. 5.6b). Performing this analysis for all the studied temperature values the temperature dependence of the spin diffusion length (Fig. 5.6b) can be determined independently from the analysis presented in Fig. 5.6a.
Figure 5.6: (a) The temperature dependence of the spin polarization, $P_c$ for the $d = 20$ nm sample. Solid and dash line show the power law fit for the spin diffusion length, $l_s$. (b) $l_s(T)$ as deduced from the exponential decay (5.2). Solid and dash lines are equivalent to those in (a). The dotted line demonstrates the saturation of $l_s$ below $T \approx 4$ K. The inset demonstrates the exponential decay of $P_c$ at two different temperatures. In order to increase the quality of the fit, the $P_0$ intersection for $d = 0$ was regarded to be the same value for all temperatures.

The resulting $l_s$ values are plotted as a function of the temperature in Fig. 5.6b. In comparison, the solid and dash lines corresponding to the power law fit in Fig. 5.6a are shown as well. It is apparent, that above $T \approx 4$ K a good agreement is found, whereas below this temperature a saturation of the spin diffusion length is observed at $l_s = 67$ nm $\pm 5$ nm. Note that this saturation could not be recovered in Fig. 5.6a for the $d = 20$ nm sample, as the spin polarization is already close to its saturation value, at such low temperatures the reduced spin polarization is only seen on the samples with larger $d$. The extrapolated $P_0 = 0.41 \pm 0.04$ is in good agreement with the results of earlier Andreev reflection measurements performed on bare Co layers resulting in spin polarizations of 0.40 $\ldots$ 0.45 [37, 86]. This agreement indicates that the spin relaxation at the Co/Pt interface does not play an important role, and the decay of the spin polarization is solely attributed to the relaxation in the Pt layer.

5.3.2 Discussion

In order to relate the measured $l_s$ to theories which usually investigate the time scale of different scattering mechanisms, the transport regime for the spin relaxation has to be found. In the ballistic regime ($\tau_m \sim t_s$), $l_s = v_FT_s$ follows. If, however, the propagation of the spin is diffusive ($\tau_m \ll t_s$), then $l_s = \sqrt{Dt_s}$ holds. Here, the proportionality factor $D$ is the diffusion coefficient that can be written as:

$$D = \frac{1}{3}v_F^2\tau_m = \frac{1}{3}v_Fl_m.$$  (5.4)
Here, $\tau_m$ is deduced by measuring the residual resistivity of a separate Pt sample of $d = 20 \text{ nm}$ thickness without the Co underlying layer. The residual resistivity of $\rho_0 = 200 \text{n\Omega m}$ corresponds to an elastic mean free path of $l_m = 4 \text{ nm}$ and a transport lifetime of $\tau_m = 1.4 \times 10^{-14} \text{s}$ follows calculating with the bulk material parameters of Pt [141,142]. Such low values are characteristic of polycrystalline thin films and show the enhanced weight of boundary scattering compared to bulk samples.

Since the spin diffusion length $l_s$ was shown to be above 10 nm in our measurements, we shall use the diffusive relation for $t_s$ and $l_s$. Moreover, as the resistivity of the sample has shown a relative variation of less then $10^{-3}$, $D$ can be regarded as constant in the temperature range of the measurements. Hence, $t_s \propto T^{-2\alpha}$ follows for the decay of the spin lifetime. The result of $2\alpha = 5.2 \pm 1.6$ for $T > 4.0 \text{ K}$ is in good agreement with the $2\alpha = 5$ value expected for electron-phonon scattering in the low temperature limit, well below the Debye temperature [63].

These results also confirm that different scattering mechanisms have different efficiency for contributing to the spin relaxation, i.e. the simple relation (2.36) of Yafet is not valid if more than one source contribute to $\tau_m$ [4]. Here, it is apparent that the electron-phonon scattering is more efficiently coupled to the spin relaxation than boundary and impurity scattering. This results in the apparent power law behavior in the $T = 4.0 \text{ K} \ldots 8.0 \text{ K}$ range regardless of the constant resistivity, i.e. constant $\tau_m$ arising from the elastic scatterings. Nevertheless, in the low temperature limit $T < 3.5 \text{ K}$, $t_s$ and hence $l_s$ saturates as well, demonstrating the role of this temperature independent background.

In this limit, the measured $l_s = 67 \text{ nm}$ corresponds to $t_s = 1.2 \times 10^{-11} \text{s}$ thus $t_s/\tau_m \approx 10^3$. At $T = 8.0 \text{ K}$, $l_s = 11 \text{ nm}$ yielding a spin lifetime of $t_s = 3.0 \times 10^{-13} \text{s}$, which is 20 times larger than $\tau_m$. This justifies the choice of diffusive transport in the entire temperature range investigated.

Care must be taken, however, when comparing our results to (2.36), where the scaling factor between $t_s^{-1}$ and $\tau_m^{-1}$ is the Fermi surface average of $b^2$, the spin mixing parameter. This simple relation was found to be in good agreement with earlier experimental data for monovalent metals [4], whereas an unexpectedly small $t_s$ was found for polyvalent materials [69]. This deviation was later explained in terms of the presence of spin hot spots on the Fermi surface in the close proximity of accidental degeneracy points and crossings of the Brillouin zone boundaries [70,143], where the spin mixing parameter $b(\vec{k})$ is much larger than the average over the Fermi surface. Such regions contribute to a broad distribution of the $b(\vec{k})$ values as shown by ab initio band structure calculations for e.g. Pt [144].

### 5.4 Conclusions of the spin diffusion measurements

In conclusion, we have demonstrated that Andreev reflection spectroscopy is a sensitive experimental probe for spin relaxation in metallic systems. By measuring the decay of the spin polarization on the surface of a thin nonmagnetic metal deposited on a ferromagnetic layer, the spin diffusion length was determined.
5.4. CONCLUSIONS OF THE SPIN DIFFUSION MEASUREMENTS

The Andreev reflection measurements can be well fitted both by the modified BTK theory and the Hamiltonian approach, giving similar results. For the Fe/Au sample a spin diffusion length of $l_s = 53\,\text{nm} \pm 6\,\text{nm}$ was found by fitting the exponential decay of the spin polarization as the function of the Au layer thickness. This value is in good agreement with the results of earlier measurements in the spin valve geometry. Nevertheless the extrapolated spin polarization $P_0 = 0.65 \pm 0.03$ of the Fe film is substantially higher than earlier Andreev reflection data for bare Fe layers. We attribute this difference to the presence of the Au capping layers in our experiments, which prevent surface degradation of the Fe layer underneath.

In order to gain an insight to the possible mechanisms of the spin relaxation, the same measurement has been performed on Co/Pt bilayer samples in the temperature range of $1.5\,\text{K} \ldots 8.0\,\text{K}$. Systematically investigating the influence of the Pt layer and the temperature on the spin polarization, two distinct regions could be distinguished. In the low temperature limit ($T \lesssim 3.5\,\text{K}$), a constant $l_s = 67\,\text{nm} \pm 5\,\text{nm}$ was found, in contrast to the decay of the spin diffusion length above this temperature reaching e. g. $l_s = 11\,\text{nm} \pm 2\,\text{nm}$ at $T = 8.0\,\text{K}$. The observed variation of $l_s(T)$ is in agreement with the prediction of the Elliott-Yafet theory, where the spin relaxation is related to the momentum scatterings mediated by the spin-orbit coupling. The power law dependence of $t_s \propto T^{-5.2}$ is consistent with that of the electron-phonon coupling well below the Debye temperature. Our results also demonstrate that the contribution of the temperature-independent background of boundary and impurity scatterings is very low, despite the apparent saturation of the resistivity of the sample well above the temperature range of our measurements.
Chapter 6
Resistive switching in the Ag$_2$S-Ag memristive system

In this chapter we present measurements and analysis concerning the Ag$_2$S chalcogenide compound. First, the details of sample preparation and characterization are presented. The influence of the preparation parameters on the electronic transport behavior of the sample is demonstrated. Thicker Ag$_2$S layers exhibit a semiconducting behavior, whereas thin ($\lesssim$ 10 nm) layers show clear metallic behavior both at room and cryogenic temperatures. Further measurements on the latter samples revealed that the reproducible resistive switching only occurs for nanometer scale junctions, whereas single atomic contacts show a rather random behavior. The former regime is further investigated by applying narrow voltage pulses, and measuring the change of the zero bias resistance directly demonstrating the nonvolatile memory operation. It is shown that the zero bias resistance can be switched even by 10 ns long voltage pulses. Finally, using Andreev reflection measurements, the creation and destruction of metallic channels is directly proved while operating the switch at low temperatures.

6.1 Sample preparation and characterization

Ag thin layers with a nominal thickness of 80 nm were deposited on an insulating Si substrate. This step was performed by the group of Dr. F. Tanczikó in the KFKI Research Institute for Particle and Nuclear Physics using molecular beam epitaxy (MBE). The following steps were performed at the Technical University of Budapest after transferring the sample in inert N$_2$ atmosphere to prevent surface contamination. The thin Ag$_2$S layer was created on the surface of the metallic layer by a low temperature sulfurization process, as follows: First, analytical grade S was loaded in a quartz tube, melted and cooled back in order to ensure a homogeneous source of subliming sulfur afterwards. The sample was then loaded in the quartz tube to a distance of 2 cm from the surface of the sulfur as shown in Fig. 6.1. The tube was then evacuated to $10^{-5}$ mbar and the temperature was rapidly ramped to 60 °C. The sublimation of the sulfur was then performed in a static vacuum (i. e. with the chamber closed off from
the pump) for a time $t_S$. As the admission of sulfur to the surface layer of the Ag thin film was performed at a relatively low temperature, the final thickness of the Ag$_2$S layer was well-controlled with $t_S$ being in the range of 1 min to 20 min.

![Diagram of sulfurization chamber](image)

**Figure 6.1:** The schematic drawing of the sulfurization chamber designed to produce Ag$_2$S samples.

The concentration profile of the samples was characterized by He-RBS (Rutherford Backscattering Spectrometry) and ERDA (Elastic Recoil Detection Analysis). The RBS and ERDA experiments were performed by Dr. E. Szilágyi at the KFKI Research Institute for Particle and Nuclear Physics supported by the Hungarian Ion-beam Physics Platform. For this characterization procedure, an ion beam of 1620 keV $^4$He$^+$ was used simultaneously at a tilt, recoil and scattering angles of 80°, 20° and 165°, respectively. An ion current of typically 4...8 nA was measured by a transmission Faraday cup [145].

The concentration profiles were determined from the acquired spectra by the RBX code [146]. In Fig. 6.2, the profile of three samples with different $t_S$ exposure times are presented. For $t_S = 20$ min (Fig. 6.2a) the sulfur penetrated the entire Ag thin film resulting in an approximately stoichiometric Ag$_2$S compound throughout the sample. In contrast, samples with shorter sulfur exposure ($t_S = 10$ min in Fig. 6.2b and 2.5 min Fig. 6.2c) exhibit inhomogeneous profiles which is consistent with the presence of a surface layer of Ag$_2$S. Note that the Ag-Si interface on all three profiles exhibits a blurriness clearly exceeding the uncertainties of the RBS analysis. This is attributed to the textured surface of the sample often observed in earlier experiments as well. The resistivity of sample a) $\rho \approx 6 \times 10^{-1} \Omega\text{cm}$ is also three orders of magnitude larger than that of sample b) and c) showing that the metallic Ag layer indeed disappeared for $t_S = 20$ min, whereas for shorter exposure times it persists providing one of the metallic electrodes of the cell. It should be noted, that the resistivity of sample a) is still orders of magnitude smaller than that of exactly stoichiometric Ag$_2$S samples [147]. The difference is attributed to the presence of excess silver in the sulfurized layer due to the low temperature preparation.

Successful experiments were also performed with Ag with a natural oxide layer after
6.2. \( I - V \) CURVE MEASUREMENTS

6.2.1 Measurement setup

Basic characterization of the surface layer was performed by recording the \( I - V \) curve of the point contacts, where one of the electrodes of the cell was the remaining Ag layer beneath the surface layer of Ag\(_2\)S. The metallic tip gently touching the surface was used as the electrochemically inert electrode. In order to test if the resistive switching effect is indeed attributed to the electrochemical reaction described in Section 2.6.2, many electrode materials, such as Au, W and PtIr were tested showing no apparent difference. Furthermore, clean samples with no Ag\(_2\)S layer on top exhibited no memristive behaviour. Therefore it is conclusive that the observed \( I - V \) characteristics are the consequence of the solid state electrochemical reaction in which Ag and Ag\(_2\)S play a vital role.

A single cycle of the \( I - V \) curve was recorded in 400 ms, which is expected to be longer than any intrinsic time constant of the device. The experiments were performed in high vacuum conditions, and at different temperature values of 4.2 K, 77 K and 300 K. Since the measurements were done in a two-probe geometry, experimental data having it exposed to air for about seven days. For this sample, RBS data have detected an areal density of 15 atom/nm\(^2\) of sulfur and 51 atom/nm\(^2\) of oxygen on the surface of the sample.

Figure 6.2: Concentration profiles of the samples of various sulfur exposure times, \( t_S \), based on the RBS and ERD measurements. Note that the penetration depth in nm is calculated assuming a homogeneous Ag\(_2\)S layer with a atomic density of \( 5.27 \times 10^{22} \text{ cm}^{-3} \). Inset shows the corresponding RBS spectra (circle) and simulation (line) at a tilt angle of 60°. The exposure times are \( t_S = 20 \text{ min (a)}, t_S = 10 \text{ min (b)}, t_S = 2.5 \text{ min (c)}, \) respectively.
6.2. **I – V CURVE MEASUREMENTS**

<table>
<thead>
<tr>
<th>sample ID</th>
<th>Conditions of preparation</th>
<th>Preparation time</th>
<th>Electronic behaviour</th>
<th>Estimated thickness of Ag$_2$S surface layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>sulfurization at 60°C</td>
<td>20 min</td>
<td>semiconductor</td>
<td>penetrated through the entire sample</td>
</tr>
<tr>
<td>b</td>
<td>sulfurization at 60°C</td>
<td>10 min</td>
<td>semiconductor</td>
<td>$\approx 40\text{ nm}$</td>
</tr>
<tr>
<td>c</td>
<td>sulfurization at 60°C</td>
<td>2.5 min</td>
<td>metallic surface layer</td>
<td>$\approx 20\text{ nm}$</td>
</tr>
<tr>
<td>d</td>
<td>under ambient conditions</td>
<td>1 week</td>
<td>metallic surface layer</td>
<td>$\approx 2\text{ monolayer}$</td>
</tr>
</tbody>
</table>

Table 6.1: The list of samples investigated in this chapter. Sample a is shown for comparison, whereas samples b, c, d exhibited resistive switching behaviour.

were compensated against the serial resistance of the driving circuit.

### 6.2.2 Composition dependence

The $I – V$ characteristics of the samples are shown to depend strongly on the preparation conditions. For sample b) the non-switching curve (Fig. 6.3a) exhibits a clear Schottky barrier behaviour which is consistent with the bulk semiconductor nature of Ag$_2$S. It should be noted that after the first switching curve (data not shown), subsequent cycles could be performed with a lower bias voltage amplitude. This is attributed to the residuals of metallic silver inside the Ag$_2$S layer after the first ON-OFF transition. This sample featured an $R_{\text{OFF}}/R_{\text{ON}}$ ratio of $\approx 100$ (see inset of Fig. 6.3b). The apparent strong temperature dependence of the switching cycle is also confirmed, no ohmic contact could be created at 4.2 K or 77 K which is consistent with the Arrhenius-type behavior (2.83).

In contrast, typical $I – V$ curves at different temperature values for sample c) are presented in Fig. 6.4. This sample exhibits linear $I – V$ curve near zero bias both at room temperature and 4.2 K. This means that the semiconductor nature of the Ag$_2$S layer does not dominate this sample, nevertheless, the presence of the layer is confirmed by RBS data discussed earlier. Notable differences to the semiconducting sample are the 1000-fold increase in the current and that the current compliance does not limit the ON state current. The $R_{\text{OFF}}/R_{\text{ON}}$ ratio is also smaller, typically in the range of 10 showing that the switching between the states is smoother compared to sample b). These result are consistent with *ab initio* calculations, revealing the presence of open conductance channels in thin Ag$_2$S layers on top of Ag due to structure relaxation [126]. The presence of such channels, i.e. metallic conductivity accounts for both the finite resistance at low temperatures and the smaller $R_{\text{OFF}}/R_{\text{ON}}$ ratio.
Figure 6.3: (a) Non-switching curve for sample b) at \( T = 300 \) K. (b) Subsequent switching characteristics on the same sample. The inset shows the absolute value of the current for the same curve on a logarithmic scale. The shift in the high resistance branch is due to the finite voltage sweep rate and decreased \((RC)^{-1}\) cutoff frequency of the measurement system.

Figure 6.4: Typical \( I-V \) characteristics for sample c) at \( T = 4.2 \) K, (a) and \( T = 300 \) K, (b), respectively.
6.2.3 Size dependence

Detailed size dependence study was performed on sample d) at $T = 4.2 \text{ K}$. In order to gain sufficient data, distinct junctions with various ON-state conductance values in the $1G_0 \ldots \ldots 400G_0$ range were investigated for switching properties. The corresponding diameter of the junctions can be estimated using Wexler equation (2.9) assuming perfect transmission through the contact. The residual resistivity of the silver thin film was $\rho = 7.2 \times 10^{-8} \Omega m$ resulting in a mean free path of $l_m = 12 \text{ nm}$. Based on these material parameters, the junction diameters vary between the single atomic size up to $\approx 10 \text{ nm}$. Typical $I - V$ curves are shown in Fig. 6.5 featuring the corresponding ON and OFF-state conductance shown in each plot.

![Typical $I - V$ characteristics measured on sample d) at $T = 4.2 \text{ K}$. The ON- and OFF-state conductance are provided for each graph in the units of $G_0 = 2e^2/h$, respectively.](image)

It is apparent that junctions with $G_{\text{ON}} = 50 \ldots \ldots 400G_0$ exhibit different properties than contacts below $G_{\text{ON}} = 20G_0$. Junctions in the first, higher conductance regime will be denoted by nanoscale junctions (Fig. 6.5a-c). Such point contacts exhibit no well-defined final states neither for the ON-state nor for the OFF-state, instead the junction conductance is tuned continuously while the bias is ramped. Note, that due to the $R_s = 90 \Omega$ serial resistance in the measurement circuit, the junction is not exactly voltage-driven, which explains the possible back-turning of the $I - V$ curve that is visible in Fig. 6.5a.
6.2. $I - V$ CURVE MEASUREMENTS

In contrast, for atomic scale junctions (Fig. 6.5d-f) with $G_{ON} < 20G_0$, well-defined initial and final states are found. This is shown by the abrupt change in the resistance resulting in a different slope in the $I - V$ curve which persists for subsequent sweep of the bias voltage until the junction switches back at an opposite bias voltage.

It is important to note that the electrochemical reaction (2.80) defines the sign of the bias voltage at which the ON-OFF and OFF-ON transition occurs, therefore it provides a well-defined direction of the switching cycle (Fig. 6.6b and Fig. 6.6c). Analyzing this property of the measurement data, together with the switching threshold voltages as defined in Fig. 6.6a, one can distinguish between physical processes that can cause resistive switching. In order to provide a complete analysis, $\approx 10^4 I - V$ curves of different junctions were measured and evaluated for these parameters.

![Figure 6.6](image)

Figure 6.6: (a) The definition of the switching threshold voltages $V_{\text{th} \pm}$. (b) and (c) The positive and the negative switching direction is defined by the polarity at which the OFF-ON transition occurs.

The distribution of the switching threshold voltages $V_{\text{th} +}$ and $V_{\text{th} -}$ are analysed in Fig. 6.7. In this colorscale plot, the relative weight of the threshold voltages are shown for each $G_{ON}$ value. The integrated distribution function for $G_{ON} > 50G_0$ and $G_{OFF} < 10G_0$ are plotted on the right and left hand side of the graph, respectively. For nanoscale junctions, well-defined threshold voltages are found. In contrast, for atomic scale contacts the distribution is broader, and goes down even to zero bias voltage contradicting the activated behaviour expected for the electrochemical reaction.

The direction of the loops was investigated as a function of the junction conductance as well. In order to quantitatively characterize this feature, we assign $+1$ for loops with a direction shown in Fig. 6.6b, and $-1$ for the opposite, shown in Fig. 6.6c. The average for each conductance bin is shown in Fig. 6.8. Here, $+1$ denotes the direction consistent with the electrochemical reaction described in Section 2.6.2, whereas, $-1$ is the opposite. The value of 0 marks that both are possible with the same probability, i.e. the direction of the loops is random. This behaviour is observed below $G_{ON} \approx 30G_0$.
6.2. $I - V$ CURVE MEASUREMENTS

Figure 6.7: Statistical analysis of the switching threshold voltages for many junctions on sample d) at $T = 4.2 \, K$. The colorscale graph shows the relative weight for a given $G_{ON}$ $V_{th \pm}$ value, whereas the histograms provide the integrated density along the conductance axes for $G_{ON} < 10G_0$ and $G_{ON} > 50G_0$, respectively.

Figure 6.8: The average direction for curves as a function of the on-state conductance. The quantity plotted is defined in the text.

...coincident with the vanishing lower limit of the threshold voltage values.

This stochastic behavior shows that in atomic scale junctions the switching process is not related to the electrochemical reaction in the Ag-Ag$_2$S system. Instead, we attribute this stochastic switching phenomenon to atomic-scale electromigration effects. This is observed as step-like changes in the conductance demonstrated in Fig. 6.9a. Furthermore, these conductance steps were statistically analyzed by creating a histogram of the individual $\Delta G = G - G_{OFF}$ conductance values for a $\approx 130$ individual traces with $G_{ON} < 10G_0$, as shown in Fig. 6.9b. Here, a clear peak around $1G_0$ is visible which corresponds to the conductance of a single Ag atom. In comparison, the push-pull histogram created by periodically indenting the tip in and removing it from the sample Fig. 6.9c, exhibited the same peak as expected.
6.3. PULSED BIAS MEASUREMENTS

Previously we have investigated the resistive switching effect by a ramped bias voltage applied on the junction, and mapped the full $I-V$ curve. A viable alternative is to apply short bias pulses and measure the resistance of the device in between. Furthermore, the response of the cell to narrow voltage pulses is especially important for possible memory applications.

Figure 6.10: The influence of alternating positive and negative bias voltage pulses on the junction resistance. The line plot merely represents the continuous sequence of the ON and the OFF states, whereas red and blue symbols denote measurement data. The experiment was performed on sample c) at $T = 4.2$ K. The pulse length and amplitude was $t_p = 100$ ns and $\pm 0.7$ V.

The permanent resistance change upon bias voltage pulses was demonstrated for sample c) at $T = 4.2$ K. The inactive electrode was a Pt/Ir 80/20 tip. In order
to achieve a permanent change in the resistance, a typical pulse amplitude in the range of 0.5 V to 1 V was used. Between the pulses a $V_{\text{meas}} = 0.1$ V measurement bias was applied, which was small enough not to influence the resistance as confirmed in e. g. Fig. 6.4a. For details, we refer to Section 3.3.4, where the timing diagram and the electronic setup for this measurement is further discussed.

Demonstrative measurement results are shown in Fig. 6.10 for a pulse length of $t_p = 100$ ns and an alternating amplitude of $V_{\text{pulse}} = \pm 0.7$ V. It is well demonstrated that after each pulse the cell undergoes a permanent resistance change that can be reversed with the next pulse applied with the opposite polarity. Furthermore, the ON- and OFF-state resistance values are well-defined, i. e. their variation is smaller than their separation. All these features make the Ag$_2$S-based memory cells a viable alternative for storing digital data in next generation memories.

Similarly to the $I - V$ curve measurements, the $V_{\text{th}}$ switching threshold voltages can be evaluated for the pulsed measurements as well. This can be achieved by applying pulses of increasing amplitude to the junction. The resistive switching is then observed via a sudden change in the zero bias resistance. Upon this transition, increasing pulses applied with the opposite sign to observe the transition in the other way around as well.

Figure 6.11: High speed pulsed measurements on sample c) at $T = 4.2$ K. The pulse width was $t_p = 10$ ns (a) and $t_p = 50$ ns (b).

Typical measurement data are shown in Fig. 6.11 for $t_p = 10$ ns and $t_p = 50$ ns pulse lengths at $T = 4.2$ K. It is demonstrated that even such short pulses are capable of generating a resistance change of an order of magnitude demonstrating a very fast memory operation even at cryogenic temperatures.

Investigating the details of the resistive switching, we first discuss the OFF-ON transition (denoted by the red arrow and red data points). Starting from the OFF-state, we find a sudden decrease in the resistance at a well-defined voltage $V_{\text{th+}}$ by ramping the amplitude of the pulses up. In this transition region, however, the bias amplitude on the
6.4. INVESTIGATION OF THE CONDUCTANCE CHANNELS

The phenomenological picture of the resistive switching in the Ag-Ag$_2$S-Me cells consists of the formation and destruction of metallic paths through the Ag$_2$S layer effectively changing the resistance of the junction. Within the Landauer formalism, such variation is caused by changing the number of the conducting channels, i.e. altering the areal contribution of the metallic channels in the junction. Alternatively, the typical transmission of the channels can be changed as well, associated with e.g. replacement of a low transmission tunnel barrier by a transparent direct metallic contact. Separating these fundamental processes could provide further insight to the physical processes contributing to the transition in resistance, which is an important information for engineering cells with favorable properties. However, merely measuring the linear conductance does not provide any information on the individual transmission values of a junction, rendering such distinction impossible.
6.4. INVESTIGATION OF THE CONDUCTANCE CHANNELS

Exploiting the fact, that Andreev reflection is a second order process, one can deduce the typical junction transmission regardless of the number of the conducting channels as discussed in Section 2.3.1 (See Fig. 2.12b and Fig. 2.12d). Here, experimental data is fitted against the BTK theory, and the $Z$ barrier strength, or the $T = (1 + Z^2)^{-1}$ barrier transmission is recovered.

6.4.1 Measurement setup

In order to make Andreev reflection measurements possible, a superconducting tip had to be used instead of the previously utilized W or PtIr. According to the scheme of the resistive switching in this system, an arbitrary superconducting electrode, which is electrochemically inert under the measurement conditions, would be suitable. We have chosen Nb due to its rigidity, and because it was well characterized in our other measurements exhibiting well-developed superconductivity. In order to confirm the resistive switching behavior, $I-V$ curve measurements have been performed (Fig. 6.12) and resulted in similar results compared to PtIr (Fig. 6.4a).

![Figure 6.12: I - V curve measurements on sample c) using Nb as the inert contact material. The data shown was taken at $T = 4.2$ K, however superconducting features emerging at the mV bias range are not expected to be visible on this voltage scale.](image)

The Andreev reflection measurements can be performed at the low bias bias region of such $I-V$ curves. Alternatively short ($\mu$s scale) pulses can be applied to switch the junction between the two states and the $I-V$ curves can be measured after each pulse. The measurements presented in this section are based on the second method, which is discussed in Section 3.3.5 in detail. Typically $t_{\text{pulse}} = 10 \mu$s pulse times were used where the resistive switching operation was found to be reliable.

6.4.2 Experimental results

Typical measurement data together with the fitted curves are shown in Fig. 6.13. Notable feature is the well-developed superconductivity, resulting in a fitted supercon-
ducting gap which is close to the bulk $\Delta = 1.55 \text{ meV}$ value \cite{29}. However typically in the OFF state an excessive smearing was found thus finite $\Gamma$ values had to be included in the fit to achieve a reasonable agreement.

\[ R_{\text{ON}} = 247 \, \Omega \quad T_{\text{ON}} = 0.519 \quad \Delta_{\text{ON}} = 1.29 \, \text{meV} \quad (\Gamma/\Delta)_{\text{ON}} = 0.11 \]

\[ R_{\text{OFF}} = 386 \, \Omega \quad T_{\text{OFF}} = 0.433 \quad \Delta_{\text{OFF}} = 1.35 \, \text{meV} \quad (\Gamma/\Delta)_{\text{OFF}} = 0.16 \]

\[ R_{\text{ON}} = 46.1 \, \Omega \quad T_{\text{ON}} = 0.722 \quad \Delta_{\text{ON}} = 1.21 \, \text{meV} \quad (\Gamma/\Delta)_{\text{ON}} = 2.2 \times 10^{-5} \]

\[ R_{\text{OFF}} = 507 \, \Omega \quad T_{\text{OFF}} = 0.493 \quad \Delta_{\text{OFF}} = 1.55 \, \text{meV} \quad (\Gamma/\Delta)_{\text{OFF}} = 0.20 \]

Figure 6.13: *Andreev reflection measurements demonstrating the change of the transmission of the junction for the ON- and the OFF-state for $R_{\text{OFF}}/R_{\text{ON}} = 1.56$ (a) and $R_{\text{OFF}}/R_{\text{ON}} = 11$ (b). Solid lines represent the fitted curves with the parameters shown.*

The change in transparency between the ON- and the OFF-state is well demonstrated both for a slight (Fig. 6.13a) and a substantial (Fig. 6.13b) change in the resistance. The fitted transmission values of $T \approx 0.4 \ldots 0.7$ show that the Ag$_2$S surface layer indeed exhibit metallic conductance which is in contrast with the semiconducting behavior of the bulk Ag$_2$S. This result directly shows that the junction is not a tunnel barrier, rather the current is flowing through direct metallic channels in the Ag$_2$S thin film. Below we will present a more detailed description of the junction conductance to further investigate the nature of switching between the two states.

### 6.4.3 Discussion

The $G_N$ normal state conductance of the junction can be expressed within the Landauer formalism:

\[ G_N = \frac{2e^2}{\hbar} \sum_{i=1}^{M} T_i \]

(6.1)

For the Ag-Ag$_2$S resistive switches a very inhomogeneous distribution of the $\{T_i\}$ values is expected ranging from $T_i \to 0$ corresponding to tunneling conductance up to $T_i = 1$ for fully transparent channels.

For the sake of simplicity we shall assume that the channels are partitioned into two groups with either a finite or essentially zero transmission:

\[ G_N = \frac{2e^2}{\hbar} (M_1T_1 + M_2T_2) \approx \frac{2e^2}{\hbar} M_1T_1 \]

(6.2)
6.4. INVESTIGATION OF THE CONDUCTANCE CHANNELS

with \( M_1 \) and \( M_2 \) are the number of conducting and tunnelling channels with an average transmission of \( T_1 \) and \( T_2 \), respectively. Further assuming that \( M_1 \sim M_2 \), i. e. the cross-section of metallic conductance is comparable to the entire cross-section of the junction, the second part is neglected. This assumption is justified by the finite average transmission values deduced from Andreev reflection measurements.

Now we consider the two limiting schemes to alter the conductance (6.2):

(i) The conducting cross-section shrinks with the average transmission being unaltered (Fig. 6.14a). This results in the decrease of \( N_1 \) effectively reducing \( G_N \).

(ii) The \( T_1 \) transmission decreases. As a result, \( G_N \) is reduced, however \( N_1 \) remains the same. This process is visualized in Fig. 6.14b.

The \( T_1 \) transmission has been evaluated by Andreev reflection measurements for each junction, and then, the number of conductance channels is determined as \( M_1 \approx G_N/(T_1 \cdot 2e^2/h) \), where \( G_N \) is the normal state conductance of the junction. In order to distinguish between the two scenarios sketched in Fig. 6.14, the variation of the fitted transmission between the ON- and the OFF-state, as well as ratio of the open conducting channels as a function of \( R_{OFF}/R_{ON} = G_{ON}^N/G_{OFF}^N \) are plotted in Fig. 6.15. Here, the limiting cases of Fig. 6.14a and Fig. 6.14b are plotted as blue and red dash lines, respectively. It is apparent, that actual measurement data scatters between these limits, hence both the conducting cross-section and the average transmission is altered when the resistive switch changes state. The dominant effect, however, is clearly the change of the number of the conducting channels, which is mostly prominent on the right side of Fig. 6.15b, where the one order of magnitude jump in resistance is accompanied by a much smaller \( T_{OFF}/T_{ON} = 1.46 \). Nevertheless, the average \( T_{OFF}/T_{ON} = 1.36 \pm 0.13 \) value marks a significant change in the transmission of the open channels as well.

Figure 6.14: Two distinct schemes for the ON-OFF transition of the resistive switch. The conducting cross-section decreases, however the transmission holds (a), the cross-section remains the same with the transmission dropping (b).
6.5 Conclusions

In conclusion, the resistive switching properties of the Ag\textsubscript{2}S-Ag memristive system has been investigated in detail. It was shown that the electronic behavior of the Ag-Ag\textsubscript{2}S sample is susceptible to the sample preparation conditions. In order to make low temperature measurements possible, samples with a metallic surface layer have to be made by the means of the sulfurization technique described earlier.

Among metallic samples, the detailed analysis of the $I-V$ characteristics as a function of the junction conductance showed that below a junction conductance of $G_{\text{ON}} \approx 30G_0$ corresponding to a diameter of $d \approx 3\text{ nm}$ the point contacts show a stochastic switching behavior instead of the well-defined switching direction and threshold voltages expected for the solid state electrochemical reaction. This characteristic change is attributed to the rise of the single atomic migration on the surface due to the extremely high current density. The scheme of random migration of the single silver atoms is consistent with our findings of step-like changes in the conductance with the prominent step size being equal to the conductance of a single silver atom.

In order to directly demonstrate the nonvolatile memory operation of the Ag\textsubscript{2}S-based cells, the junctions were biased with a narrow voltage pulse above the switching threshold. The resulting change in resistance was tracked at a lower voltage bias well below this threshold. It was demonstrated that a substantial change in the resistance occurs even for pulse lengths in the 10\text{ ns} scale. This variation was shown to be reversible by applying a pulse with the opposite polarity. The details of the resistive transitions were investigated by applying pulses with increasing amplitudes. The qual-

Figure 6.15: The variation of the open conducting channels (a) and the average transmission (b) for the ON- and the OFF-states deduced from Andreev reflection measurements. Note that a log-log scale is used in order to make the $T_{\text{OFF}}/T_{\text{ON}} > 1$ condition visible. The limiting cases of Fig. 6.14a and Fig. 6.14b are denoted by blue and red dash line, respectively.
It was shown, that by Andreev reflection measurements, in situ characterization of the junction properties can be performed. By evaluating measurement data in the Landauer formalism, we attributed the change of the cell resistance either to the change of the conducting channels or the variation of the typical transmission. Detailed analysis have shown that the dominant effect is the former one, i. e. the areal contribution of the metallic conducting regions is altered by bias voltages pulses. The fitted transmission values being in the range of $T \approx 0.4 \ldots 0.7$ are consistent with ab initio calculations [126] showing the presence of metallic conductance channels with $T = 0.455$. 
Appendix A

Calculation of the reflection probabilities in the BTK theory

We calculate the transmission and reflection probabilities for SN junctions following the theory of Blonder, Tinkham and Klapwijk (BTK) [26]. First, we consider the quasiparticle states as the solutions of the Bogoliubov-de Gennes equation [148] in the normal ($\Delta(x) = 0$ for $x < 0$) and in the superconducting lead ($\Delta(x) = \Delta \neq 0$ for $x > 0$):

$$\begin{pmatrix} H_0 & \Delta \\ -\Delta^* & -H_0 \end{pmatrix} \Psi = E \Psi.$$  \hspace{1cm} (A.1)

Here $\Psi$ is a two component spinor written in the representation of electrons and holes. $H_0$ denotes the single particle Hamiltonian. The resulting $E(k)$ quasiparticle dispersion is schematically plotted in Fig. A.1a for both leads. We assume parabolic single particle energy dispersion for the sake of simplicity, however, this assumption does not directly enter in the further calculations restricted near the Fermi edge.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{(a) The quasiparticle dispersion in the normal and the superconductor side of the junction, respectively. The possible processes denoted by $a$, $b$, $c$ and $d$ are discussed in the text. (b) The components of the wavefunction on each side of the junction, respectively. The role of the dimensionless $Z$ Dirac delta potential is discussed later.}
\end{figure}

97
The eigenfunctions at the normal side, where \( \Delta = 0 \) holds, read:

\[
\Psi_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} e^{ikx}, \quad E_1 = \frac{\hbar^2 k^2}{2m} - \varepsilon_F
\]

\[
\Psi_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix} e^{ikx}, \quad E_2 = -\frac{\hbar^2 k^2}{2m} + \varepsilon_F
\]

(A.2)

denoted as electronic and hole states, respectively, with a wavenumber of:

\[
k_{e,h} = k_F \sqrt{1 \pm \frac{E}{\varepsilon_F}} \approx k_F \left(1 \pm \frac{E}{2\varepsilon_F}\right),
\]

assuming \( \varepsilon_F = \frac{\hbar^2 k_F^2}{2m} \gg E \).

In contrast, in the superconductor, where \( \Delta \) is nonzero, we get:

\[
\Psi_1 = \begin{bmatrix} u_0 \\ v_0 \end{bmatrix} e^{iqx}, \quad E_1 = \sqrt{\left(\frac{\hbar^2 q^2}{2m} - \varepsilon_F\right)^2 + \Delta^2},
\]

\[
\Psi_2 = \begin{bmatrix} v_0 \\ u_0 \end{bmatrix} e^{iqx}, \quad E_2 = -\sqrt{\left(\frac{\hbar^2 q^2}{2m} - \varepsilon_F\right)^2 + \Delta^2}
\]

(A.3)

We note that, although the \( \Delta \) is generally a complex value, the description of SN junctions does not depend on its phase. Hence, considering \( \Delta \) a real value is valid in this case. We also made use of the BCS coherence factors:

\[
\begin{bmatrix} u_0^2 \\ v_0^2 \end{bmatrix} = \begin{cases}
\frac{1}{2} \left(1 \pm \frac{\sqrt{E^2 - \Delta^2}}{E}\right), & \text{ha } E > \Delta; \\
\frac{i}{2} e^{\pm i \arccos \frac{E}{\varepsilon_F}}, & \text{ha } E < \Delta.
\end{cases}
\]

(A.4)

Note, that now we have two solutions near the Fermi edge for each \( E \):

\[
q_{1,2} = k_F \sqrt{1 \pm \sqrt{\frac{E^2 - \Delta^2}{\varepsilon_F^2}}}. \quad \text{(A.5)}
\]

Assuming \( E, \Delta \ll \varepsilon_F \):

\[
q_{1,2} = \begin{cases}
k_F \left(1 \pm \frac{\eta}{2}\right), & \text{ha } E > \Delta; \\
k_F \left(1 \pm \frac{i\eta}{2}\right), & \text{ha } E < \Delta;
\end{cases}
\]

(A.6)

with \( \eta = \sqrt{\frac{E^2 - \Delta^2}{\varepsilon_F^2}} \).

Using the notations above, we get the resulting wavefunction on the normal side (Fig. A.1b):

\[
\Psi_N = \begin{bmatrix} 1 \\ 0 \end{bmatrix} e^{ik_e x} + b \begin{bmatrix} 1 \\ 0 \end{bmatrix} e^{-ik_e x} + a \begin{bmatrix} 0 \\ 1 \end{bmatrix} e^{ik_h x},
\]

(A.7)
and on the superconducting side:

$$\Psi_S = c \begin{bmatrix} u_0 \\ v_0 \end{bmatrix} e^{i q_1 x} + d \begin{bmatrix} v_0 \\ u_0 \end{bmatrix} e^{-i q_2 x}. \quad (A.8)$$

The four complex amplitudes $a$, $b$, $c$ and $d$ denote the possible charge conversion processes, that we have to take into account. First, $a$ is the probability of the Andreev reflection, where the final state is a reflected hole in the opposite branch. This is in contrast to the normal reflection with the amplitude of $b$, where the incoming electron is specularly reflected. The matching conditions at the interface, discussed below, demand that two transmission amplitudes, $c$ and $d$ are taken into account, with the first one resulting in a quasiparticle in the same branch, whereas the latter with branch-crossing.

Now, we employ the matching conditions of the wavefunctions at $x = 0$, where the $V(x) = U\delta(x)$ Dirac delta potential is taken into account:

$$\Psi_N(x = 0) = \Psi_S(x = 0), \quad (A.9)$$

$$\Psi'_S(x = 0) - \Psi'_N(x = 0) = \frac{2mU}{\hbar^2} \Psi(x = 0). \quad (A.10)$$

The above equation can be written in a matrix form:

$$\begin{bmatrix} 1 & -u_0 & 0 & -v_0 \\ 0 & -v_0 & 1 & -u_0 \\ i - 2Z & iu_0 & 0 & -iv_0 \\ 0 & iv_0 & -i - 2Z & -iu_0 \end{bmatrix} \begin{bmatrix} b \\ c \\ a \\ d \end{bmatrix} = \begin{bmatrix} -1 \\ 0 \\ 2Z + i \\ 0 \end{bmatrix} \quad (A.11)$$

with $Z = \frac{V}{\hbar v_F}$. After straightforward calculations, we get the unique solution:

$$a = \frac{u_0 v_0}{\gamma}$$

$$b = -\frac{Z(u_0^2 - v_0^2)(Z+i)}{\gamma}$$

$$c = -\frac{u_0(1-Zi)}{\gamma}$$

$$d = \frac{iv_0 Z}{\gamma},$$

using the notation $\gamma = u_0^2 - Z^2(u_0^2 - v_0^2)$. Here, we note that $|a(E, Z)|^2 + |b(E, Z)|^2 + |c(E, Z)|^2 + |d(E, Z)|^2 = 1$ as it is expected. Now we can evaluate the current density:

$$j = \frac{e\hbar}{m} (\text{Im}(u \nabla u) + \text{Im}(v \nabla v)), \quad \text{with } \Psi = \begin{bmatrix} u \\ v \end{bmatrix}. \quad (A.13)$$

This expression is evaluated at the normal side of the junction:

$$j = ev_F(1 + |a|^2 - |b|^2) = ev_F(1 + A - B), \quad (A.14)$$
where

\[
A(E, Z) = \begin{cases}
\frac{\Delta^2}{E^2 + (\Delta^2 - E^2)(1 + 2Z^2)} & \text{ha } |E| < \Delta; \\
\frac{\hat{u}_0^2}{\gamma^2} & \text{ha } |E| > \Delta.
\end{cases}
\] (A.15)

\[
B(E, Z) = \begin{cases}
1 - A & \text{ha } |E| < \Delta; \\
\frac{(\hat{u}_0^2 - v_0^2)Z^2(1 + Z^2)}{\gamma^2} & \text{ha } |E| > \Delta.
\end{cases}
\] (A.16)
Summary

The main conclusions of my Ph.D. work are summarized in the following thesis points:

1. I have developed a low temperature point contact measurement system utilizing the tip-sample approach. This work included the designing of the sample holder, as well as assembling different instrumental setups, suitable to measure the nonlinear $I - V$ curves of nanoscale junctions, and to investigate memory effects under very short voltage pulses, down to the 10 ns time scale. The measurement system was carefully checked for mechanical stability and was found to properly stabilize point contacts with diameters ranging in the $1 \ldots 100$ nanometer scale. I have shown, that the nonlinearities of the $I - V$ curves can be investigated with a voltage resolution down to $250 \mu V$, which is required to observe features appearing in superconductor – normal metal (SN) junctions. I have investigated the spin polarization of the current, $P_c$, in various material systems. I have evaluated measurement data both using the modified Blonder–Tinkham–Klapwijk (BTK) theory and the Hamiltonian transport model and have shown that the obtained spin polarization values agree each other within the uncertainties of the fitting procedure. Specifically, I obtained $P_c = 0.60 \pm 0.1$ for the dilute magnetic semiconductor (In,Mn)Sb, $P_c = 0.65 \pm 0.05$ for Fe and $P_c = 0.41 \pm 0.04$ for Co. The Fe and Co films were covered with a thin nonmagnetic metal layer, hence – in contrast to earlier studies – my measurements were not influenced by spurious surface scatterings [1,2].

2. I have investigated the influence of the junction diameter, $d$, on the electronic transport in superconductor – normal metal heterojunctions. Detailed experiments on the dilute magnetic semiconductor (In,Mn)Sb and its nonmagnetic counterpart (In,Be)Sb have revealed the importance of utilizing point contacts in the ballistic regime ($d \lesssim 15 \text{ nm}$) for reliable analysis of the spin polarization. For diffusive junctions ($d \gtrsim 15 \text{ nm}$), however, the larger junction diameter gives rise to mesoscopic interference phenomena resulting in a characteristic zero bias feature in the differential conductance. I have obtained a $d \approx 15 \text{ nm}$ crossover diameter for this regime which is in good agreement with the mean free path in the (In,Mn)Sb, and (In,Be)Sb samples. In addition, for the (In,Be)Sb, I have found a transition to another regime characterized by a zero bias peak sharper than the thermal smearing $k_B T$ and higher than the principal limit of $G(V = 0) = 2G_N$. 

101
of SN junctions. This feature resembles to Josephson current between two superconductors and I have related it to proximity induced superconductivity in the normal metallic lead [1,3].

3. Adopting a geometry similar to that of typical spin valve experiments, where the current flows perpendicularly to the layers, I have investigated the spin relaxation through nonmagnetic Pt and Au layers. By measuring the decay of the spin polarization on top of the thin nonmagnetic layer deposited on a ferromagnetic metal with increasing thickness, the spin diffusion length could be determined. My measurements on Fe/Au bilayers demonstrated the expected exponential decay of the spin polarization as a function of the Au layer thickness, yielding a $l_s = 53 \text{ nm} \pm 6 \text{ nm}$ at $T = 4.2 \text{ K}$. In addition, I have performed detailed studies to determine the temperature dependence of the spin diffusion length in Pt deposited on Co. Above $T \approx 3.5 \text{ K}$, a power law dependence $l_s \propto T^{-2.6}$ and a saturation in the low temperature limit at $l_s = 67 \text{ nm} \pm 5 \text{ nm}$ was obtained. Assuming diffusive spin propagation, these findings are consistent with the predictions of the Elliott-Yafet law, which attributes the spin relaxation to the momentum scatterings mediated by the spin-orbit coupling. Based on the temperature dependence of $l_s$, I have separated two contributions to the spin relaxation, the electron-phonon coupling and the temperature-independent background of boundary and impurity scatterings [2].

4. I have investigated the memristive memory cells based on the Ag$_2$S mixed ionic and electronic conductor compound. Thin Ag$_2$S layers were prepared on a silver thin film by exposing it to sulfur atmosphere at an elevated $T = 60^\circ \text{C}$ temperature. By characterizing the samples in the point contact geometry, I have demonstrated the impact of the sulfurization time on the electronic behavior. I have separated semiconducting and metallic samples, the latter exhibiting resistive switching and cryogenic temperatures as well. My results define a lower size limit of 3 nm for the reproducible switching behavior, below which a new regime emerges governed by stochastic atomic migration [4,5].

5. I have utilized Andreev reflection to characterize the average transmission and the areal contribution of the conducting channels inside the Ag$_2$S thin layer. My analysis within the Landauer formalism have demonstrated that the dominant effect is formation and retraction of conducting channels. The obtained average transmission values being in the $T = 0.4 \ldots 0.7$ range is the first experimental confirmation of earlier ab initio calculations for thin Ag$_2$S layers. In order to directly demonstrate the nonvolatile memory operation of the junctions, I applied narrow bias pulses on the cell after which the permanent change in resistance was evaluated. My results are the first experimental confirmation of the memory operation of this material system with pulse widths as narrow as 10 ns, even down to cryogenic temperatures [these results have not been published yet].
List of publications

Publications related to my Ph.D work


Miscellaneous publications

Acknowledgments

I express my gratitude to my supervisor, prof. Mihály György, who has guided me through the course of my Ph.D. work. He has provided an inspiring atmosphere in the workgroup which is of great importance for performing fundamental research. His helpful comments has greatly helped me writing my Ph.D. thesis.

I am grateful to Dr. András Halbritter, who has continuously provided invaluable help for mastering various measurement techniques and has helped me with the interpretation of the experimental results.

I acknowledge prof. Jacek K. Furdyna for providing the dilute magnetic semiconductor samples. I am grateful to Dr. Ferenc Tanczikó for preparing samples for my spin diffusion length and memristor measurements. I thank Dr. Edit Szilágyi for the RBS/ERDA analysis and the fruitful discussions.

I express my thanks for my colleagues at the Department of Physics. I am particularly grateful to Dr. Szabolcs Csonka, Dr. Miklós Csontos, András Gyenis and Péter Makk. I acknowledge the technical and administration staff of the Department of Physics for their continuous efforts.

Finally, I am greatly thankful for my family for their unending support.
Bibliography


