Chapter 1

Introduction

When man first opened its eyes, bright spots in a surrounding dark sky attracted its attentions. Restless human nature widened the vision and the knowledge. Thinking matured and raised new questions, struggling to understand Nature. Knowledge enhanced and divided into various disciplines. Different subjects started rapid development in different directions. Science stories unfolded. This one is about superconductivity and spins.

1.1 Superconductivity

The start of the twentieth century was remarkable for what is now called Condensed Matter Physics. When for the first time Helium ($^4$He) was liquefied in 1908 it led to the study of conductivity of metals at the lowest possible temperatures. Unexpectedly, the result was zero resistance in the metal Hg when it was cooled down to 4.2 K (the temperature of liquid He). It was a tremendous hidden property of the nature of the solid state that the electrical resistance could drop to zero. This observation of dissipation free conduction of current in metals is termed superconductivity and was discovered on the 8th of April in 1911 by Heike Kamerlingh Onnes [1].

Commonly, in metals the resistance $R$ decreases with temperature $T$ and saturates at a finite residual resistance $R_o$, determined by scattering of electrons on impurities and crystal imperfections. In a superconductor the resistance suddenly falls to zero below a certain temperature known as the critical temperature $T_c$. A comparison of $R(T)$ of a normal metal (in this case ferromagnetic CrO$_2$) and a superconductor (in this case amorphous Mo$_{70}$Ge$_{30}$) is depicted in Fig. 1.1. $T_c$ is material dependent and has a value around 10 K for normal metals and around 100 K for the more recently discovered high temperature superconductors [2, 3].
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The vanishing resistance is not the only special property of a superconductor. It also shows spontaneous expulsion of magnetic flux known as the Meissner effect [4], which occurs when the superconductor is cooled down through $T_c$ in an external magnetic field. Such diamagnetic behavior can be sustained in the superconductor up to a certain magnetic field known as the critical magnetic field $H_c$.

Understanding the phenomenon of superconductivity took about half a century. In 1957, Bardeen, Cooper, and Schrieffer (BCS) [5] forwarded a theory to describe the microscopic mechanism of superconductivity, where an attractive force between two electrons is required. The force of attraction is mediated via phonons (quantized lattice vibrations). Phonon interactions couple two electrons in the form of pairs, which are isolated from the normal electrons by a (zero-temperature) energy gap $\Delta(0)$. This also defines the binding energy of the pair. The binding is weak, with an energy of the order of meV’s that is usually not enough to compete with the thermal energy $k_B T$ and only wins at low temperatures. According to the BCS theory, $T_c$ and $\Delta(0)$ are connected as $\frac{\Delta(0)}{k_B T_c} = 1.74$ which is a universal number.

The electron pair (or Cooper pair) consist of two electrons with opposite momentum ($\vec{k}$-vector) and spin, and is therefore in a spin singlet state. The pair is characterized by a size or coherence length $\xi_S$, which signifies the size of the volume in which electrons are found for the pairing. Without scattering (clean limit), $\xi_S$ is given by
1.2. Superconductivity in contact with a normal metal

\[ \xi_S = \frac{\hbar v_F}{k_B T_c} \]  \hspace{1cm} (1.1)

where \( v_F \) is the velocity of the electrons at the Fermi energy. In a Cooper pair the opposite alignment of spins gives a zero magnetic moment \( (m = 0) \) and makes superconductivity incompatible to magnetic field that tries to align the electron spins.

There is another way of describing the superconducting condensate, based on the Ginzburg-Landau theory of phase transitions. In this language, the condensate is described with a single (macroscopic) wave function or order parameter, which has an amplitude and an electrons. The amplitude squared stands for the density of superconducting pairs. The phase plays a role in the description of supercurrents and magnetic flux entry.

1.2 Superconductivity in contact with a normal metal

When a superconductor (S) is brought in contact with a non-superconductor normal metal (N), Cooper pairs can leak into the N region. In terms of the order parameter, its amplitude starts to decrease within a distance \( \xi_S \) of the interface, while a finite but quickly damping amplitude is present at the N-metal side. This is called the proximity effect. The leakage of the Cooper pairs reduces the superconducting state near the interface via the inverse proximity effect which results in the reduction in critical temperature \( T_c \) in the case of thin films. In this Thesis, emphasis will be on the proximity effect rather than on the inverse proximity effect.

At the microscopic level, the proximity effect arises through the Andreev Reflection mechanism (AR) \[6\]. AR is the retroreflection of an electron with an energy below the superconducting gap \( \Delta \) as a hole. This can also be described as an incoming spin up electron and a retroreflecting spin down hole. The coherence of electron and hole can carry superconducting correlations into the N-metal. The manifestation of this process is a two-fold increase in the conductance compared to the normal state conductance. The details of this process are going to be the part of the next Chapter 2.

If the system is in diffusive limit (width is more than mean free path of electrons) the penetrating electron-hole pair in the N-metal will be out of phase (decay) within the thermal diffusion length, which is given by,

\[ \xi_N = \sqrt{\frac{\hbar D_N}{k_B T}} \]  \hspace{1cm} (1.2)
where \( D_N \) is the diffusion constant of the N-metal. This characteristic length is denoted as the coherence length in the N-metal. \( \xi_N \) at low temperatures can be of the order of a micron.

Figure 1.2: Schematical picture of the decay of the superconducting order parameter \( \psi \) as function of the distance \( x \) at (a) a superconductor-normal metal and (b) a superconductor-ferromagnet interface. The Figure is taken from Ref. [7].

1.3 Superconductivity in contact with a ferromagnet

If the N-metal is replaced with a ferromagnetic metal (F-metal) to have an S/F system, the proximity effect can still occur and a Cooper pair can penetrate into a ferromagnet, although the exchange field in the F-metal wants to break the phase coherence between the opposite spins.

The S/F interface is different from S/N interface. In the F-metal the Density of States (DOS) for spin up and spin down electrons is different at the Fermi level. Now the transport through the S/F interface is also spin dependent. Its first effect is on the AR mechanism. In the AR process an electron in the majority spin band has a lower probability to generate a retroreflected hole in the minority spin band. As a result the AR process is suppressed. The suppression of the AR channel increases with the increase in spin polarization \( P = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} \) of the F-metal, where \( N_\uparrow \) and \( N_\downarrow \) are the electron densities at the Fermi level for spin up and spin down electrons respectively [8].

When a Cooper pair from an S-metal penetrates into an F-metal as the results of AR, it dephases quickly because of the exchange field \( h_{ex} \) that tries to align the antiparallel spins of the Cooper pair, which we designate with S.
1.4 Long range proximity effect

because of its spin singlet character. The exchange field is also a measure of
the coherence length in the F-metal $\xi_F$, i.e., in a dirty limit,

$$\xi_F = \sqrt{\frac{\hbar D_F}{E_{ex}}} \quad (1.3)$$

where $D_F$ is the electronic diffusion constant in the F-metal and $E_{ex}$ is
the exchange energy coming from $h_{ex}$. Usually, the exchange energy $E_{ex}$ is
much larger than the thermal energy $k_B T_c$ so that $\xi_F << \xi_N$. The $\xi_F$ is of
the order of a few Ångströms (for a strong magnet, like Fe or Co with $h_{ex} \approx$
1 eV) and cannot be more than 10 nm even for weak ferromagnets like CuNi
or PdNi [7]. Another effect of the exchange energy is that the Cooper pair in
the F-metal gains a finite momentum, which leads to an oscillatory decaying
order parameter (see Fig. 1.2b) rather than the monotonic decay found in an
N-metal.

1.4 Long range proximity effect

In the case of an S/F interface the spin dependent DOS at the Fermi level
can give rise to spin mixing. The spin mixing is related with the Fermi wave
vector mismatch that can give different phase shifts in scattered electrons
with opposite spins. As a result, the momentum will be different for both
spin up and spin down electrons, which is responsible for generating another
component of symmetric Cooper pairs, a spin triplet with $m = 0$ ($T_0$). Looking
closer at what happens at the S/F interface, it turns out that the spin singlet
Cooper pair can be (partly) transformed into the $m = 0$ component of an
$S = 1$ triplet wave function ($|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$). There are two mechanism for this.
The fact that the Cooper pair in the F-metal has a finite momentum has a
peculiar consequence for its spin state, since both spins of the pair now start
to rotate with different frequency in the homogeneous exchange field. This can
be seen as mixing the singlet $|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$ with the $m = 0$ component $|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$
of an $S = 1$ triplet wave function. Another mechanism to generate the $m = 0$
triplet component $T_0$ is spin dependent scattering at the S/F interface. As a
result, a component $T_0$ will generally be present in the F-metal. Additional
spin rotation in an inhomogeneous magnetic field then can convert $T_0$ into
equal spin components $T_+ (|\uparrow\uparrow\rangle)$ and $T_- (|\downarrow\downarrow\rangle)$. Such inhomogeneity can come
from domain wall, non-collinear magnetization structures or even from helical
magnetic order in the F-metal. Now the Cooper pair life in F-metal comes
much easier. The spins are aligned, so the exchange field cannot break them
and the pairs can penetrate over long length: similar length, actually, as the
S Cooper pairs in a normal metal.
This is part of the basis of the Long Range Proximity effect (LPP) in a ferromagnet. There is one ingredient still missing, however. From the Pauli principle, it would seem that a spin triplet is only compatible with an odd orbital wave function, such as a $p$-wave. This would make the Cooper pair very sensitive to potential scattering by the defects in the material and be detrimental to long range effects. With $s$-wave symmetry, this issue is not present. It turns out, as was discussed by Berezinskii [9] in the framework of $^3$He, and then much more recently by Bergeret et al. [10] for the $S/F$ problem, that it is possible to have $s$-wave spin triplet correlations, since the wave functions can also be odd in time or frequency. This is the key to LRP, as will be discussed in Chapter 2.

Spin flip scattering inside the F-metal might still be a hindrance to LRP. Since the spin diffusion length $l_{sd}$ is usually much larger than $\xi_F$ of the singlet, and of the same order of magnitude as $\xi_F$ of the triplets, spin flip scattering does not seriously hinder LRP. Especially interesting, however is the case of a half metallic ferromagnet (HMF), where only one spin orientation is present at the Fermi level. Now, spin flip scattering is virtually absent and the range of the proximity effect can become very large at low temperatures.

On the experimental side, Keizer et al. [11] in 2006 claimed the observation of Josephson supercurrents induced in a thin film of CrO$_2$ (100 nm thick) which is an HMF material, with a junction of the order of 1 $\mu$m long. The half metallic nature of CrO$_2$ makes it impossible to allow $s$-wave singlet Cooper pairs to penetrate because of the total suppression of the AR mechanism. It can only be possible for Cooper pairs with the same spin ($m = \pm 1$). At the same time, Sosnin et al. [12] reported the observation of LRP effects in ferromagnetic Ho wires of lengths up to 150 nm using an Andreev interferometer geometry. No other experiments were reported for quite some time but the field was revived in 2010. We observed supercurrents in CrO$_2$ a new [13, 14], to be discussed in this Thesis; Khare et al., [15] and Robinson et al. [16], observed supercurrents in a Co over much longer lengths than the singlet $\xi_F$ and LRP effect were also seen in Co based nanowires over length of 600 nm [17].

In the experiments involving CrO$_2$, a serious issue was the reproducibility of the results, with different devices showing widely varying numbers for the critical current. Part of the issue was that films were grown and structured/measured at different locations (Alabama and Delft respectively), but more generally, it showed that the mechanism of the generation of the $s$-wave spin triplet odd frequency Cooper pairs was neither well controlled nor well understood. This will be further investigated in this Thesis.
1.5 Motivation and outline

The motivation for the work may now be clear. It is the goal of this Thesis to reproduce the observation of supercurrents in CrO\(_2\) thin films, to understand the mechanism(s) behind the generation of odd-frequency triplets, and to find a reliable method to grow samples which yield reproducible results. Film growth is a challenge in itself. CrO\(_2\) is a metastable phase which easily converts into insulating Cr\(_2\)O\(_3\), hindering the fabrication of a transparent interface. In this sense, it is a challenge to fabricate an SFS device with transparent interface. Therefore, we started with the growth of CrO\(_2\) thin films ourselves. In this way, we can fabricate CrO\(_2\) based SFS devices with better quality interface and have much freedom to investigate the properties of the interface and individually films as well. The first part of this Thesis is about the investigations on CrO\(_2\) growth and its properties.

Figure 1.3: (a) SFS junction fabricated by depositing NbTiN superconductor electrodes over CrO\(_2\) thin films with a gaps of the order of micron (b) Magnetization orientation of CrO\(_2\) film regarding to the junction (c) I-V characteristics is revealing a zero resistance branch with a critical current of the order of 50 µA at 1.6 K for junction length of 310 nm and inset shows the I-V for another junction that is illustrating the hysteretic behavior. These Fig. are taken from Ref. [11].
In Chapter 2, the basic theory of the odd-frequency spin triplet superconductivity is reviewed. A possible smoking gun experiment to find out the triplet Cooper pair generation at the S/F interface, suggested by the theory, is also discussed.

The growth of CrO$_2$ thin films via Chemical Vapor Deposition (CVD) on TiO$_2$ and sapphire substrates is discussed in Chapter 3, along with focus on the morphology of the films, their crystallography, and their magnetic properties. The results are discussed in the context of growth conditions, types and pretreatment of substrates.

Our main type of measurements are transport, so, the transport properties of CrO$_2$ thin films are studied and discussed in Chapter 4, where temperature dependent resistivity $R(T)$, anisotropic magnetoresistance (AMR), angular dependent magnetoresistance (MR($\theta$)), Planar Hall effect (PHE) and Anomalous Hall effect (AHE) are discussed for CrO$_2$ thin films deposited on different substrates.

Chapter 5 gives the main results with respect to generation of triplet superconductivity. This is observed in CrO$_2$ thin films deposited on sapphire substrates. We cannot find any supercurrent when the films were deposited on TiO$_2$ substrate unless we deposit 2 nm thick Ni layer prior to the deposition of superconducting leads. Our observations indicate that the magnetic inhomogeneity like multi-axial anisotropy of the films can help to generate a T Cooper pair out of S Cooper pair. It can also be done for a uniaxial ferromagnetic thin films like CrO$_2$ thin films deposited on TiO$_2$ substrate along with an other ferromagnetic thin film of the thickness of the order of coherence length $\xi_F$.

Something different but not totally out the context of this Thesis, is presented in Chapter 6. Where magnetothermoelectric power (MTEP) measurements are given, measured on various thin films like Py, Co and CrO$_2$. MTEP has a close correlation with anisotropic magnetoresistance and/or MR and CrO$_2$ showed a huge signal for MTEP.

As discussed above that Co has also been used to investigate the the odd-frequency spin triplet superconductivity with pillar shaped Josephson junctions. For such junctions, it is a hindrance to estimate the upper limit of the coherence length for triplets because of the limitations of thickness of Co layer. With this objective, we tried to fabricate the Co based junctions in lateral geometry and observed the signatures of long range proximity effect over the junction length of 130 nm. The preliminary results are discussed in Appendix A.

The resistance verses temperature for CrO$_2$ based devices show an unexpected sharp up-jump at the critical temperature $T_c$. This effect is also de-
scribed in Chapter 5 but some more investigations are given in the Appendix B.

Appendix C is describing the control experiments in the context of possible short in the junctions. Confidently, we cannot see any possible short in our devices to provide a weak link between two superconducting pads except CrO$_2$ itself.