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Superconductivity and ferromagnetism, despite their inherent competing nature, can be combined. The result of the marriage is the emergence of novel phenomena such as, for example, odd-frequency spin triplet superconductivity. Moreover it offers the basis to develop a new and powerful technology which makes use of spin and superconducting properties, called superspintronics.
# Contents

1.1 Superconductivity and ferromagnetism .......................... 3  
1.2 Coexistence of superconductivity and ferromagnetism ....... 4  
1.3 Odd-frequency long-range proximity effect ................... 5  
1.4 From spintronics to superspintronics ........................... 7  
1.5 Motivation & outline ........................................... 9
1.1 Superconductivity and ferromagnetism

Since the dawn of time nature has never stopped to amaze us with its complexity and its creativity. And it typically does so at two levels: first at the macroscopic scale, where a physical phenomenon manifests itself more or less directly to the eyes of the observer, provoking a sense of marvel for something not expected or unusual. Such marvel Heike Kamerlingh Onnes must have felt on October the 4th, 1911, when in his laboratory in Leiden, he first saw the electrical resistance of a sample of mercury dropping to absolute zero. It was the discovery of superconductivity. The second level is the microscopic one, at atomic and subatomic scales. In this microscopic world, much more difficult to access, we can find the ingredients to describe the mechanisms responsible for the macroscopic phenomena. These mechanisms are often complex and require a certain degree of abstraction but they unveil the beauty of nature, if possible, even more. Scientists have the privilege to have a closer look at this world.

It took more than fifty years before Bardeen, Cooper and Schrieffer succeeded in unveiling the microscopic mechanism which describes low-temperature superconductivity. According to their model\(^1\), when a superconductor is cooled below its so-called critical temperature, the electrons start to feel an attractive force, mediated by lattice vibrations, and they pair up in pairs, commonly known as Cooper pairs. In conventional (singlet) Cooper pairs the two electrons have opposite momentum (the total angular momentum is zero) and, in order to fulfill the Pauli principle, opposite spin (total spin \(S = 0\)). All the pairs behave like bosons and condense in a single ground state. Thus, not only is there an interaction between the electrons within the pair, but all the Cooper pairs interact with each other as a whole, forming the superconducting condensate. This picture becomes more clear if we consider the quantum-mechanical particle/wave duality: the sea of Cooper pairs can be seen as a single state where all the (waves associated with the) electrons behave in a coherent way. This collective state, protected by an energy gap, is impervious to impurities and defects and therefore it is not subjected to dissipative processes. In other words, in the superconducting state the electrons cooperate together so that it is not possible to disturb (excite) a single electron separately, unless the energy is larger than the energy gap. As a consequence, the electric (super)current travels undisturbed, with zero resistance. Besides being a perfect conductor, a superconductor is also a perfect diamagnet: when cooled down below its critical temperature any magnetic field present inside the supercon-

\(^{1}\)The model, called BCS theory, is only valid for conventional superconductivity. The mechanism for the high-\(T_c\) superconductors is still under debate.
ductor is expelled and cannot penetrate the interior of the superconductor (Meissner-Ochsenfeld effect).

For the reasons explained above, superconductivity is an example of a phenomenon where the macroscopic behavior is a direct expression of the purely quantum mechanical character of the many-electron state. Another, equally fascinating, example is ferromagnetism. In a ferromagnet, the exchange interaction amongst electrons on neighboring atoms makes it energetically favorable for their spins to be aligned parallel. As a result, the bulk material has a net magnetic moment, sum of all the individual magnetic moments. While the ferromagnetic phenomenology has been known for more than two thousands year, the role of the exchange energy, a pure quantum-mechanical effect, was introduced by Heisenberg and Dirac only in 1926.

Superconductivity and ferromagnetism, thus, share similarities in their collective nature which makes them of particular interest also for several applications. However, there is a fundamental difference between the two states: while for the superconducting pairing the spins of the electrons have to be aligned antiparallel, the exchange energy forces the spins to be parallel. This inherent competing nature poses the question whether superconductivity and ferromagnetism can be combined and what happens if one tries. Fortunately the answer is yes, and in the next sections we will see how. The result is not only the coexistence but the emergence of totally new and unique phenomena.

1.2 Coexistence of superconductivity and ferromagnetism

The exchange energy is not the only mechanism which tends to suppress superconductivity. The other one, introduced by Vitaly Ginzburg who first addressed the problem of the coexistence in 1956, is the orbital effect: pair breaking is also caused by the interaction with the internal magnetic field of the ferromagnetic state, which exerts a different Lorentz force on the two electrons with opposite spin. However, the exchange energy is typically much stronger and therefore it is dominant on the orbital effect. Similarly to what happens when an external magnetic field is applied, the exchange energy (as the Zeeman energy) splits the energy levels for parallel and antiparallel spin states, making the former much more favorable.

Despite that, superconductors with coexisting ferromagnetic order, have been found. Examples of such ferromagnetic superconductors are $\text{UGe}_2$ [1], $\text{URhGe}$ [2] and
1.3. Odd-frequency long-range proximity effect

UCoGe [3], where the electrons undergo both types of ordering at the same time, or ErRh$_4$B$_4$ [4] and Ho$_6$Mo$_6$S$_8$ [5], where the two states alternate in a modulated fashion as function of the temperature.

But the coexistence can also be observed with less exotic materials, for instance in the vicinity of the interface between a conventional superconductor (S) and a ferromagnet (F) in S/F bilayers. When crossing the S/F interface, the Cooper pairs arrange themselves in a so-called FFLO state$^\text{ii}$ On the ferromagnetic side the exchange energy $E_{\text{ex}}$ shifts the energy levels of the spin-up and spin-down electron bands, with a total difference equal to $2E_{\text{ex}}$. In order to adjust to the Fermi level, the two electrons forming the Cooper pair shift their momenta, and the pair acquires a nonzero center-of-mass momentum. This momentum makes the spin singlet component $|\uparrow\downarrow - \downarrow\uparrow\rangle$ mix with the spin triplet component $|\uparrow\downarrow + \downarrow\uparrow\rangle$. This mixed state gives rise to interesting effects and physical phenomena but it is short ranged, meaning that the triplet component decays over the same length scale as the singlet component. Thus, even though the FFLO state allows the Cooper pairs to survive in the ferromagnet this is possible only within a small region close to the interface. The typical length scale of the penetration of the superconducting state is given (in the dirty limit$^\text{iii}$) by the coherence length

$$\xi_F = \sqrt{\frac{\hbar D_F}{E_{\text{ex}}}}, \quad (1.1)$$

where $\hbar$ is the reduced Planck constant and $D_F$ is the diffusion coefficient of the electrons in the ferromagnet. The exchange energy value $E_{\text{ex}}$ for standard ferromagnets such as Co, Ni and Fe is of the order of an eV, so typical $\xi_F$ values do not exceed 1-2 nm. Obviously, for the development of applications this short range is not appealing. In fact, as we will see in the next section, the scenario described above is only part of the story because, under particular conditions, it is possible to have a long-range proximity effect.

### 1.3 Odd-frequency long-range proximity effect

Searching for the possibility of long-range effects, about fifteen years ago it was realized that if the Cooper pair is somehow converted to the triplet state with spin parallel $|\uparrow\uparrow\rangle$, then it is no longer affected by the exchange-energy breaking and can survive

$^\text{ii}$after the name of its discoverers R. Flude and Ferrell on the one side and, independently, A. Larkin and Y. Ovchinnikov.

$^\text{iii}$In the dirty limit the electronic mean free path $l$ is the shortest length after the Fermi wave length $\lambda_F$. 
longer inside the ferromagnet. The question is how to generate such triplet Cooper pairs. Indeed, all the standard superconductors have singlet pairing with only a few exceptions. Amongst these there are Sr$_2$RuO$_4$, UPt$_3$ and some other heavy fermion systems, where the superconductivity stems from correlations between 4$f$ and 5$f$ electrons. But triplet superconductivity can be \textit{induced} in a S/F bilayer made by a standard singlet superconductor. The mechanism was proposed for the first time in 2001 by the theoretical work of Bergeret et al. [6]. The key ingredient for generating the equal-spin triplet component is to provide inhomogeneous magnetization at the S/F interface. We have already seen that, at the interface, the triplet component with magnetic quantum number $m_s = 0$ (\(|↑↓ + ↓↑\rangle\)) is generated. While the singlet component is rotationally invariant, \(|↑↓ + ↓↑\rangle\) is not. In the presence of magnetic inhomogeneities, this triplet component is rotated in spin space and converted to the spin-parallel triplet component (\(m_s = \pm 1\)). When this happens, the Cooper pair can survive over a much longer range, with the length scale now determined by

$$\xi^T_F = \sqrt{\frac{\hbar D_F}{k_B T}},$$

(1.2)

with $k_B$ the Boltzmann constant and $T$ the temperature. At low temperature $k_B T$ is much smaller than $E_{ex}$ so $\xi^T_F$ is much bigger than $\xi_F$, and can reach the $\mu$m scale. An important limiting factor, not included in the formula, is the spin diffusion length, which basically sets the length scale over which the electrons preserve their spin. Indeed, once equal-spin triplets are created, any scattering event which does not conserve the spin, breaks the Cooper pairs. For standard ferromagnets the spin diffusion length, so $\xi^T_F$, is tens of nm (60 nm for Co), while for 100% spin-polarized half-metals, such as CrO$_2$, $\xi^T_F$ can be of the order of a $\mu$m.

The fact that this parallel-spin triplet component can exist at all is not trivial. The electrons forming a Cooper pair have to fulfill the Pauli principle, which is equivalent to saying that they have to obey fermionic statistics. This means that the total wave function, product of the spatial-orbital part and the spin part, has to be antisymmetric, namely odd under the exchange of the two electrons. With the triplet-pairing the spin part is symmetric, so in order to satisfy the requirement, the orbital part has to have an odd parity. This is true for all the cases mentioned above, as examples of systems where triplet superconductivity is "naturally" present. The orbital part is here \(p\)-wave (or \(f\)-wave, even if more rare). This scenario is however not compatible with S/F diffusive systems. A \(p\)-wave orbital coupling, which is anisotropic, is extremely sensitive to scattering (in particular potential scattering from defects) and cannot exist over a long range in presence of disorder.
Is then equal-spin triplet coupling completely forbidden in a diffusive systems? No, if we also consider the time (frequency) dependence of the wave function. The only possible candidates for a long-range propagation in a standard ferromagnet are odd-frequency $s$-wave spin-parallel triplet Cooper pairs. For a deeper understanding of the meaning of odd frequency we would need to go into details of the quantum mechanical formalism, but an intuitive picture can be given if we consider that a direct consequence of the wave function $\Psi$ being odd under the exchange of the time variables of the two electrons, $t_\uparrow$ and $t_\downarrow$, is that $\Psi(t_\uparrow = t_\downarrow) = 0$. In other words the Pauli principle is not violated because the two electrons do not occupy the same state at the same time. In the big "sea" of the Cooper pairs there is an uncertainty in the time information of the single electrons (coherently with the basic principles of quantum mechanics) and therefore in the time of the coupling.

This type of pairing does not exist in any known material and is unique for S/F hybrid structures. It is one of the many examples in physics where the combination of two different materials, or systems, does not simply result in the sum of the properties of its components but gives rise to completely different and novel phenomena. For this reason the study of S/F hybrids is very interesting from a fundamental point of view. Beside that, the study is very appealing for possible applications: it gives us the possibility of combining the properties of ferromagnetism (spin), already widely exploited in the available technologies, with the advantages offered by superconductivity, such as zero dissipation and nonlocality. This can result in a completely new type of electronics, with the promise of much improved performance: superconducting spintronics.

1.4 From spintronics to superspintronics

The building blocks of standard electronics, the elements in which the single bits are stored, are metal-oxide-semiconductor field-effect-transistors (FETs). Without going into details of the working principle, it is sufficient to know that in every transistor the information is stored in the dielectric as charge accumulation, or capacitance: a read/write process means inducing (or not) this charge accumulation (write) and measure whether the accumulation is or is not present (read). In the past decades the semiconductor technology has developed at an astonishing pace, by improving performances and pushing the miniaturization more and more. The level achieved so far is impressive, with areal densities of the order of a Tbit per square inch. However the transistor scaling is reaching its physical limit and there are issues which have
to be challenged for further improvement. In an ideal device one is seeking for high density storage, fast read/write process, low power consumption and non volatility, namely that the information is not lost when the power is shut off. The most traditional technologies for information storage, already introduced more than 20 years ago, are dynamic access memory (DRAM) and flash memory. An intrinsic problem of the transistors they are made of, is that the dielectric suffers from charge leakage. For this reason the device has to be refreshed every few ms, making the DRAM a volatile memory. In Non Volatile Random Access Memories (NVRAM), by using a “floating gate” - a metallic island embedded in a thick dielectric - the information is stable even after the power is switched off. But because of the thickness of the dielectric, the time for charging and discharging (reading and writing) are very long, up to ms. Furthermore in all the capacitative devices, the durability is limited to about $10^5-10^6$ [7] cycles because the dielectric deteriorates.

Two promising technologies that can potentially surpass semiconductors are spintronics and superconducting electronics. Superconducting electronics has demonstrated switching frequencies in the THz range, but circuit complexity and integration density are low because of the physical size of the elements required to contain one flux quantum ($2 \times 10^{-15}$ Wb), which translates to micrometer length scales.

The term spintronics, on the other hand, indicates all the technologies that exploit the spin information of the electron [8]. The way for the use of spin properties in the electronics was paved by the discovery of the giant magnetoresistance (GMR) effect by Fert and Grünberg in 1988. They found that in a stacked trilayer where two ferromagnets are separated by a nonmagnetic layer, there is a "giant" variation of the electrical resistance if the magnetizations of the ferromagnetic layers are switched from parallel to antiparallel alignment. The difference between the two resistive states - typically of the order of several tens percent - is exploited for many applications. Examples are hard disk drives; bionsensors or microelectromechanical systems (MEMS), where the GMR effect is used as magnetic field sensor; or the Magnetoresistive Random Access Memory (MRAM) where the GMR device is used as single bit, in which the antiparallel and parallel states are the 0 and 1 of the logic. GMR-based device performances were surpassed by MTJs (Magnetic Tunneling Junctions) devices, in which the metal layer is substituted by an insulating layer. In this case the magnetoresistance effect can reach up to several hundreds percent.

MTJ-based devices offer many advantages. Because the information is determined by the magnetic state of the ferromagnetic layers, the state is non-volatile, very fast switchable (order of ns), with a durability almost infinite (up to $10^{15}$ cycles) and power
efficient (by a factor $10^3$-$10^5$ respect to standard RAMs [7]). In conventional MRAM memories the writing is typically performed by a local Oersted magnetic field generated by an array of wires through which an electric current is passed. The magnetic field partially influences the neighbor bits, setting some limitations on the efficiency and the areal density. One alternative way to locally manipulate the spin of a single bit is via Spin Transfer Torque (STT): a spin polarized current with sufficient current density can exert a torque on the weakly pinned magnetization of a ferromagnetic layer, modifying its alignment. Furthermore, this technology can be implemented with pure spin currents (zero net charge current), so very low dissipation. The spin manipulation only requires a small amount of energy; however, in standard magnetic materials, large charge currents are required to generate sufficiently large spin current, which causes considerable Joule heating.

It is becoming clear where the ability of generating spin-polarized triplet superconductivity can play a role. We can have dissipationless spin polarized currents which can exploit the intrinsically low switching energies and high switching frequencies of spintronics. Moreover, it is of great interest for the possibility of introducing quantum-coherence phenomena in spintronics devices. The entanglement and non-locality of triplet Cooper pairs, for example, can offer the basis for the development of quantum computers.

## 1.5 Motivation & outline

The importance of studying triplet superconductivity in S/F hybrid structures has become clear in the previous sections. A detailed understanding of the mechanisms which regulate triplet generation and injection is still far from being reached but many steps forward have been realized in the past decade.

After the theoretical proposal by Bergeret et al. [6] in 2001, the first experimental evidence was given by Keizer et al. [9] in 2006. The breakthrough experiment unequivocally showed that in a lateral S/F/S Josephson Junction the two superconducting layers could be coupled through several hundreds nm of ferromagnetic CrO$_2$. These first measurements were confirmed by Anwar et al. [10] for lengths up to 700 nm. The only possible explanation for such long range proximity effect was that singlet Cooper pairs had been converted into the equal-spin triplet component. In these devices the magnetic inhomogeneities, key ingredient for the spin rotation and the triplet generation, were related to the misalignment of the magnetic moments of the different domains in CrO$_2$. The intrinsic misalignment does not allow a control of the magnetization and
so of the generation. Moreover it affects the reproducibility of the mechanism which relies on the randomness of the remanent magnetic state.

It was quickly realized that much more reliable results could be obtained by engineering the magnetic inhomogeneities, by adding an extra ferromagnetic layer F’, called mixer layer, between the S and F layers. The non-collinearity of magnetization between F and F’ (typically very thin) can be controlled by applying a magnetic field or simply by shape anisotropy. The Josephson junction becomes now of the type $S/F’/N/F/N/F’/S$, with N a normal metal simply used to decouple the magnetization of the F and F’ layers. The first work introducing an extra mixing layer was by Khaire et al. [11] in 2010. It was also the first time that a long range proximity effect was shown through the conventional ferromagnet cobalt, for thicknesses up to 30 nm. Several experiments followed, confirming long-range proximity in different junctions based on Co [12] or CrO$_2$ [13] with an F’ layer and addressing the optimization of different parameter of the structures. In particular in the experiment of Robinson et al. [12] the rare earth metal holmium, peculiar for its helical magnetization, was used as spin mixer. In the case of holmium the misalignment in the magnetization, necessary for the singlet-to-triplet conversion is then intrinsic in the material.

This was the state of the art about induction of odd-frequency superconductivity in a ferromagnet when the work on this thesis started. It was clear that triplet Cooper pairs could be created in S/F hybrids albeit many questions about the control of the mechanism were still open. One of these, for example, was about the possibility of making lateral junctions based on Co. The junctions based on CrO$_2$ were in a lateral geometry, with gap size defined by the distance between the superconducting electrodes, while all the Josephson junctions based on Co were in a vertical stack with the gap given by the thickness of the ferromagnet. A lateral Josephson junction has the advantage that the gap can be varied by controlling the distance between the superconducting contacts so with no limitation in the maximum length which can be probed, while in vertical junctions increasing the thickness of the ferromagnetic layer could lead to problems of inhomogeneity. Moreover a lateral configuration can be better implemented in electronic circuit for device applications.

This thesis tries to explore the mechanism of singlet-to-triplet conversion to answer the following questions. How can we quantify the efficiency of the singlet-to-triplet conversion? What is the role of the interface transparency? Is it possible to generate triplets by exploiting the intrinsic magnetic non collinearity in domain walls? Can other transition metal magnets be used besides Co, such as the well-known soft magnetic alloy Ni$_{80}$Fe$_{20}$ (permalloy)? The outline is then as follows.
1.5. Motivation & outline

In Chapter 2 we introduce some fundamental theoretical concepts about superconductivity, proximity effect, odd-frequency triplet superconductivity and ferromagnetism.

In Chapter 3 we present a detailed study of the magnetic properties of permalloy, from which emerges the existence of a new inhomogeneous magnetic configuration, hitherto not described, in a particular range of permalloy thickness. This regime, that we called emerging stripe domains (ESD), is of particular interest for us because it can offer the right condition for triplet superconductivity.

In Chapter 4 we investigate the possibility of generating triplet superconductivity by means of intrinsic magnetic inhomogeneities. For that we investigated Superconductor/Ferromagnet/Superconductor trilayers and Superconductor/Ferromagnet bilayer films with Nb as superconductor and permalloy in the emerging stripe domain regime as ferromagnet, looking at the behavior of the critical field as function of temperature.

In Chapter 5 we present our results on triplet spin valves (TSVs), based on half-metallic CrO$_2$. The triplet spin valve effect results in a “colossal” variation of the critical temperature of the superconductor, up to more than 1 K. Furthermore the experiments highlight the crucial role played by interface transparency, and the thickness of the mixer layer.

The same triplet spin valves are studied in Chapter 6 but now looking at a different quantity: the critical field. In our particular geometry, the study of the behavior of the critical field seems to be a more fundamental way to characterize the triplet spin valve effect.

In Chapter 7 we investigate the Josephson effect in planar Superconductor/Normal Metal/Superconductor junctions where a thin ferromagnetic layer is added at the bottom of the normal metal. Due to the exchange pair-breaking of the ferromagnet, the supercurrents induced into the Normal Metal/Ferromagnet weak-link result strongly suppressed, compared to the Superconductor/Normal Metal/Superconductor case.


