Chapter 2

The physics of superconductor-ferromagnet hybrids

This chapter is concerned with a number of general notions on the physics of superconductor-ferromagnet hybrids, the Long Range Proximity (LRP) effect, and the choice of the ferromagnet for the experiments. It is divided in the following sections. Section 2.1 gives a sketch of the quasi-classical theory which describes such observables as the Density of States (DOS) and the critical current in an S/F proximity system. Section 2.2 focuses on the conditions to have a finite critical current carried by spin triplets in an S/F/S junction and Section 2.3 looks more closely at the role of spin active interfaces. The last Section 2.4 gives a number of characteristics of the half metallic ferromagnet CrO$_2$, which is the main material of choice for the experiments on the LRP effect.
2.1 Theoretical concepts: triplet superconductivity

In Chapter 1, we discussed the superconducting proximity effect with an F-metal even though both superconductivity and ferromagnetism are antagonistic in nature. The exchange field in the F-metal will try to align the opposite spins of a Cooper pair and as a result the pair will dephase within the coherence length, which in F-metals is not more than few nanometers. The previous chapter also introduced the Long Range Proximity (LRP) effect which can occur in an SFS structure similarly to SNS structures. The LRP effect in an F-metal is created by the generation of equal spin triplet Cooper pairs at the interface between the S-metal and the F-metal, which requires a magnetic inhomogeneity. Such a Cooper pair is not sensitive to the exchange field and can exist in a diffusive system over a length of the order of micrometers. A conventional triplet Cooper pair however would require $p$-wave orbital symmetry and be very sensitive to disorder, thereby disallowing LRP. This can be circumvented by the notion of odd-frequency pairing. As we discussed in Chapter 1, it is our main objective to generate such so called odd-frequency spin triplet superconductivity in self-fabricated SFS devices, where the F-metal can be a half metallic ferromagnet like CrO$_2$. To understand the properties of such devices, it is necessary to gain some understanding of the theory of the proximity effect, especially in ferromagnetic metals.

Such theory describes the energy and space dependence of normal electrons and holes, as well as superconducting correlations, with as outcome measurable quantities such as the Density of State (DOS), or the electrical current ($I$). This (quasi-classical) theory builds on the expectation values of the functions $g = \langle \psi(x, t)\psi^*(x', t') \rangle$, and $f = \langle \psi_\uparrow(x, t)\psi_\downarrow(x', t') \rangle$. Here, $\psi(x, t)$ annihilates an electron at position $x$, time $t$, and arbitrary spin, while the operator $\psi^*(x', t')$ creates it at $(x', t')$. The function $g$, called the single-particle Green’s function of the system, therefore describes the average of possible paths of the electron. Similarly, the function $f$ (called the anomalous Green’s function or the condensate function) describes the Cooper pairs. Since the reservoir of the Cooper pairs is formed by the electrons, $f$ and $g$ are related by $f^2 = g^2 - 1$.

In terms of the single particle energy $\epsilon$, the condensate function is given by,

$$f(\epsilon) = \int dt f(t - t') \exp \left[ i\epsilon((t - t')) \right]$$

(2.1)

and the DOS for instance is given by the real part of the single particle Green’s function:

$$r(\epsilon) = \text{Re } g(\epsilon)$$

(2.2)
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Staying for the moment with equilibrium situations (no currents), the strength of the formalism lies in the fact that diffusion-like equations can be written for \( f \) and \( g \), which are not limited to the superconductor. Hybrid system with S, N or F layers can be coupled through suitable boundary conditions, and with the S-layer as the source of the superconducting correlations. The DOS can then be found anywhere in the system. The equation which is appropriate for dirty systems (characteristic lengths larger than the mean free path) is the Usadel equation:

\[
\hbar D \left[ f \nabla^2 g - g \nabla^2 f \right] + 2i [\Delta g + \epsilon f] = 0 \tag{2.3}
\]

where \( \Delta \) is the superconducting pair potential, which is related to \( f \) by a self-consistency equation: \( \Delta = \lambda f \), with \( \lambda \) is the strength of the electron-electron interaction. On the N-side of an S/N interface, we can assume that \( g \) is constant and \( \Delta = 0 \), so that Eq. 2.3 takes the form,

\[
D_N \nabla^2 f = -2i \epsilon f \tag{2.4}
\]

The solution is the exponential decay of \( f \) on the N-side with a characteristic length \( \sqrt{\frac{\hbar D_N}{\epsilon}} \), where \( D_N \) is the diffusion constant of normal metal. Since the relevant energies are of the order of \( T \) (temperature), this gives rise to the definition of the normal metal coherence length \( \xi_N = \sqrt{\frac{\hbar D}{kT}} \). Note that this length is actually different for correlations with different energies. It can be very long, of the order of micrometers at low temperature (up to inelastic relaxation length).

Two extensions now should be considered. One is the way to use the formalism to compute non-equilibrium properties, in particular the currents in the system. For this, also time-reversal states of the system play a role as well as the so-called Keldysh function, which controls the filling of one-particle states in the out-of-equilibrium situation. This will not be further described although several results will be quoted later. The other extension is to convert the N-metal into an F-metal and consider the S/F system. Basically, this means adding an exchange field \( h_{ex} \). If the exchange field is small, we need not to consider the different spin subbands, but the condensate function becomes more elaborate, since now the spin space plays a separate role. It turns out that \( f \) become a matrix \( \hat{f} \) with two components:

\[
\hat{f} = f_3 \hat{\sigma}_3 + f_o \hat{\sigma}_3 \tag{2.5}
\]
2.1. Theoretical concepts: triplet superconductivity

Here, $f_3$ is the amplitude of the singlet component and $\hat{\sigma}_3$ is the Pauli-matrix along the $\hat{z}$-axis, which is also the direction of $h_{ex}$. The other term is new. It signifies the presence of a spin triplet component (amplitude $f_o$), which has zero projection on the $\hat{z}$-axis; in other words, it is the $m = 0$ or $(\uparrow \downarrow + \downarrow \uparrow)$ component of a triplet. It should be emphasized that the simple form of Eq.2.5 is only valid for the case of homogeneous magnetization ($h_{ex}$ is independent of the coordinates). In the F-metal, the condensate function is then described by

$$D_F \nabla^2 \hat{f}_F + 2i(\epsilon \hat{\sigma}_3 + h_{ex} \hat{\sigma}_3) \hat{f}_F = 0 \quad (2.6)$$

which reverts to Eq. 2.4 for $h_{ex} = 0$. The solutions of this equation are of the form,

$$f \propto e^{-x/\xi_F} \left[ \cos \left( \frac{x}{\xi_F} \right) \pm isin \left( \frac{x}{\xi_F} \right) \right] \quad (2.7)$$

with $\xi_F = \sqrt{\frac{\hbar D_F}{h_{ex}}}$. It brings out two known characteristics for S/F systems; the condensate function damps fast, since the exchange field wants to align the spins in both components; but it also oscillates. This give rise to the physics which has been developed over the last decade, of oscillatory $T'_c$s in S/F multilayer and phase changes as a function of the F-layer thickness which can lead to so called $\pi$-junctions [18–22]. So far, however, there is no LRP effect.

As a matter of fact, it is not even clear yet that LRP could exist. If so, it is obvious that such a condensate function should have an $m = \pm 1$ ($\uparrow \downarrow$ or $\downarrow \uparrow$) component, in other words, that it should be a spin triplet. In itself, the existence of a spin triplet in a superconductor is not forbidden. There is a restriction, however, with respect to the possible condensate functions or order parameters. Just as for the wave function making up a singlet Cooper pair, the order parameter $\Delta(r)$ or correlation functions of the form $\langle \psi_\alpha(x, t) \psi_\beta(x', t') \rangle$ (here, $\alpha$ and $\beta$ are spin indices) are subject to the Pauli principle. This says that the wave function or order parameter, which can be written as the product of a spatial part and a spin part, is antisymmetric with respect to permutations of the coordinates and the spin of the particles. A spin singlet therefore requires a spatial or orbital even symmetry. This can be $s$-wave as in all classical superconductors, or $d$-wave as in high $T_c$ materials such as YBa$_2$Cu$_3$O$_7$. As a consequence, such an order parameter is anisotropic, with so-called nodes in the gap function along different crystal directions and with different phases in different parts of $k$-space. A spin triplet requires an orbital
odd symmetry, such as \( p \)-wave, which is found in \( \text{Sr}_2\text{RuO}_4 \) \[23\]. Such a \( p \)-wave condensate is very sensitive to the presence of impurities and the material in this case has to be very clean. An \( s \)-wave condensate would not show such sensitivity, but according to this reasoning, an \( s \)-wave spin triplet cannot exist. This is not correct, however, as was already pointed out by Berezinskii \[9\] in the framework of a theory for superfluid \( ^3\text{He} \). The Pauli principle for a condensate function such as \( \langle \psi_\alpha(x, t)\psi_\beta(x', t') \rangle \) is strictly valid for equal times \( t = t' \), but equal times are not strictly needed to generate a non-zero average. This is better seen by Fourier transforming them. This is called the Matsubara representation, which writes the earlier Green’s functions, as well as the present correlation functions, in terms of a sum over frequencies. The formal trick here is to consider a Heisenberg operator \( e^{iHt/\hbar} \) (with \( H \) a Hamiltonian), then consider the imaginary time \( t = it \), and purely formally identify this with an inverse temperature \( T^{-1} \). In this way, the transform of \( f(t - t') = f(\tau) \) becomes \( T \sum e^{i\omega_n \tau} f(\omega_n) \), with \( \omega_n = (2n + 1)\pi k_B T \) the Matsubara frequencies. The sum over \( n \) is taken to a cut-off frequency such as the Debye frequency \( \omega_D \). This condensate function \( \langle \psi_\alpha(x, t)\psi_\beta(x', t') \rangle \) is then written \( \sum_n \langle \psi_\alpha(x, \tau)\psi_\beta(x', \tau) \rangle \). If this sum is to represent a spin triplet, it must be an odd function of coordinates or zero. But it can also be an even function of coordinates if it is an odd function in \( \omega \); in terms of an order parameter: \( \Delta(\omega) = -\Delta(-\omega) \). In this way, \( s \)-wave spin triplets are allowed without violation of the Pauli principle. All together, the different pairing possibilities are summarized in Table 2.1.

Then one final question remains, namely how to generate the odd frequency \( s \)-wave triplet. Here, a crucial role is played by an inhomogeneous magnetization at the S/F interface. Historically the first suggestion for this came from Bergeret et al. \[10\] who considered the structure shown in Fig. 2.1a in which an S reservoir is connected to an F-bar of length \( L \). Over a length \( w \) of this bar the exchange field rotates, described by a rate of rotation \( Q \), so that the local angle is given by \( \alpha = Qx \). What then happens is that a projection of the spin is locally zero \( (m = 0) \), but finite at a position where \( h_{ex} \) is rotated. Practically, it is an example of the domain wall at the interface. In a simple way the magnetization in the F-bar can be written in the following way,

\[
\begin{align*}
\alpha &= Qx & 0 < x < w \\
\alpha &= \alpha_w & x > w
\end{align*}
\] (2.8)

where \( \alpha \) is the angle of the magnetic moment with the \( x \)-axis (along the ferromagnetic wire). If \( Q = 0 \) the magnetization is homogeneous at the in-
Table 2.1: The Table shows the different possibilities for Cooper pairs along with their possible examples of existence. The last row is the Cooper pair with odd-frequency that can exist in an S/F hybrids.

<table>
<thead>
<tr>
<th>Cooper Pair type</th>
<th>Spin</th>
<th>Orbit</th>
<th>Time (Frequency)</th>
<th>$V(r_1, r_2)$</th>
<th>Examples of occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singlet</td>
<td>Odd</td>
<td>Even, L=0</td>
<td>Even</td>
<td>Odd</td>
<td>Conventional Superc.</td>
</tr>
<tr>
<td>Singlet</td>
<td>Odd</td>
<td>Even, L=2</td>
<td>Even</td>
<td>Odd</td>
<td>HTc Cuprates</td>
</tr>
<tr>
<td>Triplet</td>
<td>Even</td>
<td>Odd, L=1</td>
<td>Even</td>
<td>Odd</td>
<td>$^3$He, Sr$_2$RuO$_4$</td>
</tr>
<tr>
<td>Triplet</td>
<td>Even</td>
<td>Even S-wave</td>
<td>Odd</td>
<td>Odd</td>
<td>S/F interface</td>
</tr>
</tbody>
</table>

In the result only the $m = 0$ odd-frequency triplet component penetrates into the F-metal over the length of $\xi_F$. This component is also induced in the S-metal within $\xi_S$. For finite values of $Q$ the magnetization is inhomogeneous, which results in the generation of $m = \pm 1$ spin triplet Cooper pairs. Such pairs are found together with spin singlet pairs within the penetration length of singlets, but penetrate beyond $x = w$ in a normal metal, as shown in Fig. 2.1b. Here, a difference between the odd-frequency triplet superconductivity suggested by Berezinskii and suggested by Bergeret can be seen. In the former case spin triplet Cooper pairs exist with an $\omega$-dependent pair potential $\Delta(\omega)$ but in latter case, both spin singlet and triplet can exist with an order parameter independent of $\omega$.

The inhomogeneous magnetization can also modeled differently, with an F/S/F structure, where the F-layers have a magnetization angle of $\pm \alpha$ with respect to the $z$-axis and the S layer is not thicker than $\xi_S \propto \sqrt{D_S/T_c}$ ($D_S$ is the diffusion constant in the S-metal). For homogeneous magnetization and parallel or antiparallel alignment of the magnetizations of the F-layers, only the $m = 0$ triplet component is generated at both interfaces and penetrates into the S layer. For non-collinear magnetizations, however, all possible spin triplet (0, ±1) Cooper pairs are generated. The amplitude of the $m = \pm 1$ triplet is reduced with the increase in the thickness of the S layer.
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Figure 2.1: (a) A schematic of an SF device where an F-bar of length $L$ is connected to a superconducting block. The magnetization rotation is shown above the structure as a linear rotation of the magnetic moment with rate $Q$ up to a length $w$. Such a situation can be found in reality with a magnetic domain wall at the interface. (b) The superconducting order parameter in the F-layer as a function of the penetration length along the $x$-axis. The singlet part has oscillating behavior and is short range, while the triplet part can penetrate over a long range up to $L$ for the chosen angle $\alpha_w = \pi/5$. This Figure is taken from Ref. [10].

2.2 Critical current density in $S/F_L/F/F_R/S$ junctions

The final part of this discussion concerns the critical currents ($I_c$) in $S/F$ based proximity structures. Of particular interest is a structure of the form $SF_LFF_RS$, suggested by Houzet and Buzdin [24]. Here all three F layers have a homogeneous magnetization, but with the left (right) one rotated over an angle $\varphi_L$($\varphi_R$) with respect to the middle one as shown in Fig. 2.2a. In such a device, a conduction electron will experience the following exchange field [24],

$$h_{\text{ex}}(y) = \begin{cases} h_o (\sin(\phi_L \hat{x}) + \cos(\phi_L \hat{z})) & \text{if } 0 < y < d_L \\ h_o \hat{z} & \text{if } d_L < y < d_L + d \\ h_o (\sin(\phi_R \hat{x}) + \cos(\phi_R \hat{z})) & \text{if } d_L + d < y < L \end{cases}$$

This structure can illustrate the influence of the non-collinear magnetiza-
2.3. Spin active interfaces

tion on the supercurrent, which consists of a singlet part $I_{cs}$ and a triplet part $I_{ct}$. The expression for the singlet component is

$$eI_c R_N = \frac{\pi}{2\sqrt{2}} \frac{\Delta(T)}{k_B T} \frac{d}{\xi_F} \sin \left( \frac{\pi}{4} \pm \frac{d}{\xi_F} \right) e^{-\frac{d}{\xi_F}}$$

(2.9)

where $R_N$ is the interface resistance, $d$ is the thickness of the central F-layer, and $\xi_F = \sqrt{\hbar D/h_{ex}}$. This is the well-known oscillatory damped critical current. The triplet component follows from,

$$I_{ct} = -I_{cN} \frac{d}{\xi_F} \frac{d^2}{L^2} \sin \psi_L \sin \psi_R$$

(2.10)

where $d_{L(R)}$ is the thickness of the left (right) layer, and the amplitude $I_{cN}$ actually is the critical current of an S/N/S junction:

$$eI_c R_N = 2\pi k_B T \sum_{\omega > 0} \frac{q_o d}{\sin hq_o d} \frac{\Delta^2}{\omega^2}$$

(2.11)

with $q_o = \sqrt{2\omega/\Delta}$. This formulation stresses the similarity between an S/N/S junction and an S/triplet-F/S junction, but even more importantly, it shows that the magnetizations on both sides of the central F-layer need to be non-collinear in order for a supercurrent to exist.

This is made clear in Fig. 2.2b taken from Ref. [24], which shows the effects of magnetization rotation on the critical current for different thicknesses $d_L = d_R << d$. The angle $\varphi_L$ is fixed at $\pi/2$, while $\varphi_R$ is rotated between $-\pi/2$ and $\pi/2$. The value of $I_c$ is maximum when the magnetizations at both interfaces are antiparallel but perpendicular to the central layer; the same value is reached when the magnetizations are perpendicular to the central layer but parallel to each other, but now the current is negative, signifying that the junction is in a $\pi$ state. When the magnetization on the right side is parallel to the central layer, $I_c$ is zero even though inhomogeneous magnetization on the left interface still provides the condition for a triplet. Experimentally, this model with non-collinear magnetizations has been utilized by Khaire et al. [15] and Robinson et al. [16] when measuring the supercurrent through ferromagnetic Cobalt.

2.3 Spin active interfaces

In the above discussion, two possible experimental situations generated the LRP effect mediated via $m = 1$ triplet Cooper pairs: magnetic inhom-
Figure 2.2: A schematic of an SFFFS Josephson junction consisting of three different F-layers. The central F-layer of thickness $d$ has a fixed magnetization aligned parallel to the $z$-axis, while the magnetization in left(right) layer of thickness $d_L$($d_R$) can rotate in $x-y$ plane at angle $\varphi_L$($\varphi_R$). (b) Critical current versus thickness of left(right) F-layer normalized with $\xi_F$, when $\varphi_L$ is fixed at $\pi/2$ and $\varphi_R$ is rotated between $-\pi/2$ to $\pi/2$. (Taken from Ref. [24])

eigenities like a magnetic domain wall and the non-collinear magnetization between adjacent F-layers. Both mechanisms do not describe the microscopical phenomenon of spin mixing, e.g. conversion of a singlet Cooper pair into a triplet Cooper pair at the interface. This question was addressed by Eschrig et al. [25, 26] in his calculations for SFS devices, in particular for an F-metal of half metallic ferromagnet (HMF) like CrO$_2$. It is presumed that a HMF-layer is sandwiched between two superconducting layers as shown in Fig. 2.3a. The magnetization in the bulk of the HMF-layer is along the $z$-axis but in the interface region it is distorted with respect to the bulk magnetization. In this device, the singlet order parameter (or current density $J_{\text{singlet}}$) is reduced to zero at the interface, while the triplet order parameter (or the current density $J_{\text{triplet}}$) is created at the interface and at its maximum in the half metallic
F-layer. Eschrig explains the mechanism of conversion of singlets into $m = 1$ triplets as consisting of two steps, spin mixing (spin rotation) and spin flip scattering (broken spin rotational symmetry) at the interface. An interface that exhibit both of these properties is known as a spin active interface. In previous examples, the interfaces can be considered spin active, if the domain wall width $w$ is very short and the product of $Qw = 1$; or if the thickness of right(left) layers are of the order of their coherence length. In this case, the spin activity is controlled by the angle between the magnetizations of adjacent layers.

The interface can also be spin-active, however, when scattering electrons with opposite spin experience different phase shifts because of spin dependent DOS on the F side. In this way an $m = 0$ spin triplet can be generated at the interface and penetrates into S-layer over a coherence length of S-metal. So, spin rotation at the spin-active interface mixes the $m = 0$ singlet Cooper pairs and the $m = 0$ triplet Cooper pairs due to different precession direction of moving spin up and spin down electrons. Mathematically, these rotations are expressed by $|↑⟩_{-k} = e^{iθ/2} |↑⟩_{k}$ and $|↓⟩_{-k} = e^{-iθ/2} |↓⟩_{k}$, with $θ$ the precession angle. Thus, the incoming quasiparticle with wave vector $k$ pairs with an outgoing quasiparticle with wave vector $-k$. Therefore, a Cooper pair $|↑⟩_{k} |↓⟩_{-k} - |↓⟩_{k} |↑⟩_{-k}$ transforms into another pair $e^{iθ} |↑⟩_{k} |↓⟩_{-k} - e^{-iθ} |↓⟩_{k} |↑⟩_{-k}$ which results into a combination of $|↑⟩_{k} |↓⟩_{-k} |↓⟩_{k} |↑⟩_{-k}$ $(m = 0$ spin singlet) and $|↑⟩_{k} |↓⟩_{-k} + |↓⟩_{k} |↑⟩_{-k}$ $(m = 0$ spin triplet).

Additionally, if spin-flip scattering exists at S/F interface, equal spin $m = ±1$ triplet Cooper pairs are generated. The spin flip scattering or broken spinrotation symmetry comes from the misalignment of magnetic moment at the interface with respect to the orientation of the magnetization in the bulk of the F-layer. It can be enhanced with the local variations of magnetic moments at the interface or by spin disorder (see the bottom part of Fig. 2.3b). For weakly spin polarized F-metals, such disorder or misalignment of magnetic moments cannot be significant for generating $m = ±1$ triplets although the $m = 0$ triplets can be generated. But it is an important factor to generate spin triplet Cooper pairs at the interface with a HMF layer, where only the triplet component $|↑↑⟩$ can penetrate.

Of final interest is the anomalous behavior found in the calculation of the temperature dependent of the critical current $I_c(T)$. The anomaly is a characteristic peak appearing at very low temperature. The temperature of the peak $T_{peak}$ depends on the coherence length and the length of the junction. The observation of such a peak can be a smoking-gun experiment to give an independent proof of the existence of odd-frequency spin triplet superconductivity.
2.4 Chromium dioxide (CrO$_2$)

Pure stoichiometric CrO$_2$ is a metallic ferromagnetic oxide with unique properties. It has a Curie temperature $T_c$ in the range of 385 - 400 K [27]. The Cr ions are in the Cr$^{4+}$ state with the electronic configuration [Ar]3d$^2$ and have a magnetic moment of 2 $\mu_B$ per ion. CrO$_2$ has a rutile structure, described by a bcc tetragonal unit cell with lattice constants $a = b = 0.4419$ nm and $c = 0.2912$ nm. There are two Cr ions in the cell, at positions (0,0,0) and ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). The four oxygens are at $[u,u,0]$ and their symmetric equivalents, where $u = 0.303$. The oxygen atom form octahedra around the Cr-atoms, and are both side-sharing and corner-sharing. The side-sharing octahedra form a kind of ribbons along the $c$-axis [28] (slightly distorted, elongation along $c$-axis) [29, 30], as shown in Fig. 2.4.

Chromium dioxide became technologically important when in 1956 DuPont
found a way to fabricate CrO$_2$ nanorods using the decomposition of CrO$_3$ in the presence of water at pressure of more than 2000 bar and a temperature $\approx 480$ °C. The properties of these particles are an extremely high aspect ratio (shape anisotropy), a high remanent magnetization and good adhesion to suitable media for use in magnetic recording.

Figure 2.4: The CrO$_2$ rutile crystal structure, illustrating the orientation of the oxygen octahedra and the perpendicular ribbons, aligned parallel to the crystallographic $c$-axis. This Figure is taken from Ref. [30].

A novel feature of CrO$_2$ was found in 1986, when electronic band structure calculations proposed that it belongs to the class of half metallic magnets [31, 32], i.e. it has a gap in the minority spin DOS at the Fermi level of the order of 1.5 eV, but no gap in the majority DOS, resulting in complete spin polarization at the Fermi level. These predictions, and the discovery of giant magnetoresistance (GMR) which started a new field of research called Spintronics, (where the spin of electrons is exploited rather than the charge), added interest in CrO$_2$ for use as a source of spin polarized current.

The Cr ion in its formal 4+ valence state has two electrons in $t_{2g}$ orbitals with spin quantum number $S = 1$. As mentioned, it is a HMF, although a Mott insulating-like ground state and antiferromagnetic spin order could be expected because of strong correlations. Kroton et al. [29] showed using the LSDA+U method that the $d$ bands of CrO$_2$ are divided into two parts: a
Figure 2.5: The density of state for majority (↑) and minority spins (↓) in CrO$_2$. A gap in the minority ($\Delta_\downarrow$) spin bands is present at the Fermi level to make it a half metallic ferromagnet (taken from the Ref. [29]).

weakly dispersing band well below the Fermi level and a strongly dispersing band crossing the Fermi level. The former band provides the localized moments and the latter is a strongly $s$–$d$ hybridized band that dilute the effect of the $d$–$d$ Coulomb interaction and is responsible for the metallic behavior in CrO$_2$. The spin-dependent DOS calculated with LDA+U is shown in Fig. 2.5.

The elongation of the CrO$_6$ octahedra yields a natural basis for a local coordinate system for the $t_{2g}$ orbitals, namely $xy$ and $(yz \pm zx)$. Here, the $z$-axis is directed to the apex oxygen. The oxygen 2$p$ state extends to the Fermi level and provides the electron or hole reservoir. This causes self doping and double exchange between the $d$-electrons.

The CrO$_2$ surface is thermodynamically unstable under atmospheric conditions with a tendency to decompose to the insulating antiferromagnetic and more stable phase Cr$_2$O$_3$ ($a = 4.951$ Å; $c = 13.566$ Å; space group: R3c, $T_N = 393$ K) [33, 34]. Measurements of optical properties revealed that this process is accelerated at temperatures above 200 °C [34]. That is why deposition is very sensitive to the variations in oxygen pressure, flow rate and substrate temperature. The metastable state of CrO$_2$ makes it impossible to use low pressure conventional deposition techniques like sputtering, molecular beam epitaxy (MBE) or pulsed laser deposition (PLD). Still, high quality films can be grown by Chemical Vapor Deposition (CVD) at ambient pressure,
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where a precursor such as CrO$_3$ is thermally evaporated and the sublimated precursor transfers to a lattice matched substrate (such as TiO$_2$ or Al$_2$O$_3$) at an elevated temperature of 390 °C using a pure Oxygen flow. The details of the CVD technique are given in Chapter 3. Electrical transport measurements on single crystalline CrO$_2$ showed that it is a bad metal at a room temperature (specific resistivity of the order of 500 $\mu\Omega$cm) but metallic at lower temperatures with a residual resistivity of the order of 10 $\mu$Ωcm.

CrO$_2$ is a better choice to use as a HMF than NiMnSb, or Fe$_3$O$_4$. NiMnSb is a Heusler alloy and 100% spin polarized but the Fermi level is close to the band gap edge of the minority spin bands. Fe$_3$O$_4$ has spin down as majority spin band at the Fermi level, while the spin up band has a gap of 0.5 eV, but it cannot be used because of a Verwey transition at 122 K, changing the band gap and the conductivity; at lower temperatures the resistivity increases rapidly to become insulating and a smaller gap also starts to open for the spin down (majority spin) bands. Another possibility would be HMF La$_{0.7}$Ca$_{0.3}$MnO$_3$ or La$_{0.7}$Sr$_{0.3}$MnO$_3$. These materials have been studied in combination with the high-$T_c$ superconductor YBa$_2$Cu$_3$O$_7$ (without LRP), but the main problem will be to avoid insulating magnetic oxides to form at the interface.