PROBING THE SUPERCONDUCTING ORDER PARAMETER OF IRON-BASED SUPERCONDUCTORS THROUGH THE JOSEPHSON EFFECT

BY

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DISSERTATION

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Abstract

We report the results we obtained regarding the use of the Josephson effect to probe the symmetry of the superconducting order parameter of Co-doped Ba(FeAs)$_2$ crystals (Ba122). This measurements were carried out to test the validity of the s± model, which predicts the pairing in the multiband Ba122 compounds being mediated by the exchange of spin excitations, with the condition that the electron and hole bands in the superconductor’s Fermi surface have opposite signs. Josephson interferometry applied using Pb/Cu/Ba122 SNS structures in corner/edge junction configurations shows two distinct $I_c\Phi$ patterns that support an anisotropic s-wave superconducting gap. The use of $I_cR_N$ data favors the hypothesis of the gap anisotropy being in direct connection to an electron gap having an opposite sign when compared to the hole gaps in the material. Finally we considered the prediction of proximity-induced changes in the density of states of a thin film of a conventional superconductor due to the presence of a Ba122 crystal. Our results found evidence of both a positive and a negative proximity effect, which in conjunction with other features identified in the density of states spectrum of the thin film of conventional superconductor, points strongly towards the legitimacy of s± model.
A mi familia: Irma, Juan Miguel y Adrián: mis pilares, mi andar y mi energía.
I would like to acknowledge the help I have received from all the people that crossed my path in the years I have spent in this beautiful community. In first place, I say thank you to my families: to my biological family in Mexico, to which I owe everything I have become, for walking with me everywhere I go and teaching me that I am never alone and that we are all just a flight away; to my family in Champaign-Urbana, from which I got my now older brother Bris, for giving me the support that I needed whenever I needed it, whether it was through a warm sancocho or a sincere word next to a bonfire; and to my i’ich and permanent accomplice, Sarah, who has shown me that the subtleties of the everyday-humanity can sometimes overwhelm any kind of certainty that the scientific sphere can provide; there we can find the ideas that truly define us as human and let us shine as such.

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long life, the best music and a big dance floor. I hope I can come back to share some dance steps with them in the not-so-far-away future.

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<th>Abbreviation</th>
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<tr>
<td>Ba122</td>
<td>Superconductor based on the parent compound Ba(FeAs)$_2$, with either electron-, hole-, or isovalent doping.</td>
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<tr>
<td>FeSC</td>
<td>Iron-based superconductors</td>
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<tr>
<td>AntiFM</td>
<td>Antiferromagnetic</td>
</tr>
<tr>
<td>SDW</td>
<td>Spin-density–wave</td>
</tr>
<tr>
<td>FS</td>
<td>Fermi surface</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin Zone</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting Quantum Interference Device</td>
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<tr>
<td>AFM</td>
<td>Atomic-Force microscopy</td>
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Chapter 1

Introduction

The discovery of superconductivity in 1911 [1] primed the study of how quantum-mechanical effects combined with crystal structures could affect drastically the electronic behavior of certain materials. When Ginzburg and Landau [2] presented their phenomenological theory of superconductivity (GL) and, later, Bardeen, Cooper and Schrieffer developed a their microscopic theory of superconductivity, now known as BCS [3], a wave of successful predictions on the electromagnetic properties of existing superconductors arrived.

The GL theory describes superconductivity based on observation and can be derived from microscopic theories like BCS, however, it makes no assumptions in regards to the origin of them observed phenomena; GL only makes distinctions between normal electrons and superconducting electrons. According to GL, we can treat a superconductive transition at a temperature $T$ close to $T_C$ as a second order phase transition, for which a free energy density function $\mathcal{F}$ can be constructed. Since for most phase transitions a process of ordering can be identified, an order parameter $\Psi_{\text{GL}}$ is defined such that $\Psi_{\text{GL}}^* \Psi_{\text{GL}} = n_{sc}$. After BCS, we make the definition of $n_{sc} = n_p = \frac{1}{2} n_s$; here, $n_{sc}$ refers to the effective density of superconductive electrons, $n_p$ and $n_s$ are the effective density of paired charges and single charges respectively, although when GL was developed, there was still no indication that charges suffered a pairing process when superconductors undergo their phase transition.

The creation of this GL order parameter $\Psi_{\text{GL}}$ as a complex number with magnitude and phase, allowed the descriptions of supercurrents\footnote{Dissipation-less currents created by the flow of paired charges in the superconductor} wherever there was winding in the characteristic phase of $\Psi_{\text{GL}}$, or spatial alterations in the pairing density through changes in the magnitude of $\Psi_{\text{GL}}$. From this theory, a set of parameters characteristic to all superconductors was redefined: the London penetration depth, $\lambda_L$, that characterizes the typical length over which a magnetic field will be expelled from the surface of a superconductor; and the superconducting coherence length $\xi$, that characterizes the typical distance over which the superconducting electrons maintain their phase coherence.

When BCS was developed as a candidate microscopic model for superconductivity, it tried to address the problem of the condensation of all superconducting charges into a state described by $\Psi_{\text{GL}}$. Cooper had
already stated that an attractive potential could pair up electrons in the Fermi sea, even if that potential was weak \[4\] but it wasn’t until BCS that the premise of an attractive potential based on the interactions between single electrons and the crystal lattice around them could be developed. Through this theory, the individual electrons form bosonic entities, which can later condense in a single quantum-mechanical state.

From this perspective, the ground state in the superconductors described by BCS is a spin-singlet state where single electrons of opposite spin and momentum are effectively paired, giving rise to the so-called \textit{Cooper pairs}. All the pairs formed by electron-phonon interactions can be described by a single quantum-mechanical phase, resulting in long-range microscopic phase coherence. This two effects combined make supercurrents very resilient to localized non-magnetic impurities and scattering sources, indeed keeping them dissipation-less.

One of the predictions of BCS is the existence of an energy gap $\Delta$ that determines the energy cost of the creation/ destruction of a Cooper pair. In the theory, it is established that $\Delta \sim |\Psi_{\text{GL}}|$ and that, for conventional superconductors, $\Delta(k)$ is nearly an isotropic quantity in $k$-space. This kind of superconductive pairing is called s-wave pairing, in analogy to the spatially isotropic electronic states in materials. The BCS predictions matched the observations on conventional low-temperature superconductors like Aluminum (Al), Lead (Pb) and Tin (Sb) and could be directly matched to the descriptions from GL theory.

Up until the early 1980’s, the experimental research in the synthesis of superconductors resulted in materials with higher $T_C$ and critical current densities ($J_C$), backed up by the understanding of the pairing mechanisms provided by BCS. However, with the discovery of cuprate superconductors in 1986 \[5\], the idea of a non-BCS Cooper pairing became a reality and a controversy started on the origin of the unconventional superconductivity in these 2-dimensional compounds.

Cuprate superconductors started the family of High-\(T_C\) superconductors and are formed from perovskite-like structures based on CuO$_2$ planes coupled by weak Josephson coupling with other elements between them. Upon doping with interstitial oxygen, parent compounds transition from a Mott insulator into type-II superconductor. Their $T_C$’s are unusually high compared to the superconductors previously discovered, with the highest being 133 $K$ from HgBa$_2$Ca$_2$Cu$_3$O$_8$. The extremely high $T_C$ in conjunction with very short coherence lengths $\xi_0$, rule out electron-phonon interaction as the main pairing mechanism, forcing us to rethink our understanding of the phenomenon of superconductivity.

The search for more High-\(T_C\) superconductors after the cuprates led to new fruition in 2008, when Hosono \textit{et al.} \[6\] discovered the superconducting transition in La[O$_{1-x}$F$_x$]FeAs. With it, there was the surge of a renowned effort to understand the mechanisms behind unconventional pairing and its symmetry properties for all these Copper oxide-based and Iron-based unconventional superconductors (FeSC).
In order to enter a stage where more superconductors can be designed rather than accidentally discovered, the scientific community is pressed to answer the question about the mechanisms behind the association of electrons into Cooper pairs and the symmetry properties of the order parameter $\Psi$. Our hope is that new paradigms will result in materials with higher critical temperatures ($T_C$) and higher critical current densities ($J_C$), opening the way for more applications to everyday life. Thus, the characterization of $\Psi$ and its symmetry in newly discovered superconductors is of high relevance.

In this thesis I present the work done towards the characterization of the superconducting order parameter in Co-doped Ba(FeAs)$_2$ crystals in an effort to elucidate their characteristic pairing symmetry and to test the validity of current models, like the $s\pm$ model, as accurate descriptions of the electron dynamics in these systems.
Chapter 2
Iron-based superconductors

2.1 Background

In order to understand the behavior of Fe-based superconductors (FeSC), one must first analyze its basic building block, the FeAs plane. This plane starts with a square lattice of Fe atoms with a Fe-Fe distance of approximately 2.6 Å; the As atoms reside on the center of that square, above and below the Fe plane[7]. It has been argued that the angles and spacings between Fe and As atoms are essential to the rise of superconductivity and it has been seen empirically that the highest $T_c$ occurs when the FeAs planes form a regular FeAs$_4$-tetrahedron [8, 9].

![Crystal structure of different families of Fe-based superconductors](image)

Figure 2.1: Crystal structure of different families of Fe-based superconductors. Under each family, the most representative compound and its maximum $T_c$ is shown. Figure taken from [7].

Shortly after their discovery, as many as 6 distinct families of FeSC could be identified. Table 2.1 shows the typical parent compounds for each family and the maximum registered $T_c$.
In describing the characteristics of FeSC, it would be useful to compare them first to the cuprate superconductors. At first glance, both families of superconductors share some structural characteristics. Their similarities can be summarized in the following way:

a. Both cuprates and FeSC’s require doping to become superconductive.

b. In the same way FeSC base their structure in the FeAs plane, cuprate superconductors base their structural composition in the CuO$_2$ planes.

c. Both FeSC and cuprates include transition metals in their structures.

d. A high-temperature orthorhombic transition is present at low dopings in both superconductors. Anti-ferromagnetic (AntiFM) ordering can be tied to the occurrence of this transition.

e. Electrons from d-orbitals in both materials dominate the Fermi surfaces, and thus, mediate the rise of superconductivity.

Nevertheless, there are some very important differences between these two types of materials that bring them into separate families:

a. At room temperatures, the parent compounds in cuprates are Mott insulators, while in FeSC’s they are metals.

b. FeX (X = As, P, Se, Te) planes in FeSC’s form regular tetrahedrons, whereas CuO$_2$ planes are almost 2-dimensional [11].

c. Doping in FeSC’s can be done directly on the active pairing layer while in cuprates, doping is done interstitially.

d. The AntiFM ordering in cuprates disappears rapidly with doping, however in some FeSC compounds, there seem to be coexistence between this magnetic ordering and superconductivity, giving us evidence even of a quantum critical point [12, 13].

e. In cuprates, the d$_{x^2−y^2}$ orbital from the Cu atoms dominates the FS, creating a single band superconductor, however, As atoms in FeAs planes have d-orbitals that hybridize strongly with d-orbitals from...
Fe atoms, creating a multi-band superconductor [14].

For the purposes of these thesis, we will center our attention in the 122 family of compounds, of which, $Ba(FeAs)_2$ (Ba122 from here on) is the parent compound. In this family there are 3 major compounds that represent the different ways that superconductivity is obtained in these materials from doping: $Ba(Fe_{1-x}Co_xAs)_2$ which is electron-doped, $Ba_{1-x}K_x(FeAs)_2$ which is hole-doped and $Ba(FeAs_{1-x}P_x)_2$ which is isovalently-doped.

The undoped Ba122 compound exhibits a resistivity at 300K of 430$\mu\Omega$cm, relatively high for metals, with a marked anisotropy between the a-b plane and the c-axis $\rho_c/\rho_{ab} \sim 150$ [15]. The resistivity anisotropy changes significantly with doping, reaching values of $\rho_c/\rho_{ab} \sim 2 - 5$ for the optimally Co-doped Ba122 [16].

The Ba122 family (as with most FeSC’s) goes through a structural transition from paramagnetic tetragonal to orthorhombic at a temperature $T_s \sim 100K$. There is then the onset of antiferromagnetic (AntiFM) ordering in coexistence with the orthorhombic structure at a $T_{N_{e\chi}} < T_s$. This transitions can easily be seen in magnetic susceptibility and heat transport measurements [17]. In contrast with cuprates, where the AntiFM ordering is conventional (adjacent spins are aligned antiparallel to each other), undoped FeSC parent compounds exhibit a stripe order with an arrangement consisting of spins of a chain of nearest neighbors in the Fe plane ferromagnetically oriented, combined with the perpendicular chain of nearest neighbors in the Fe plane showing an AntiFM orientation. This resembles strongly the type of ordering called a Spin-Density–Wave (SDW) [18]. Quantum oscillation experiments on the 122 family are consistent with DFT calculations showing AntiFM ground state involving quasiparticles in a SDW model [19].

For the case of the parent compound, the AntiFM order persists all the way to $T = 0$ and the accepted scenario is that doping favors superconductivity by weakening the AntiFM state just enough to permit Cooper pairing. Figure 2.2 shows the phase diagram of the 3 main sub-families in the Ba122 structure. In these phase diagrams we can see the evolution of the AntiFM state with doping.

The electronic structure of FeSC’s is required to understand the interesting properties that can be seen in the bulk. Using Density Functional Theory (DFT) and, particularly, the Local Density Approximation (LDA) [20, 21], the band structure of FeSC’s has been calculated for several of the parent compounds across the different families. The results indicate that the hybridization of the $d$-orbital electrons from the FeAs planes create 5 distinct bands, 3 of them hole-like and 2 of them electron like, that cross the Fermi surface (FS) creating hole-like and electron-like pockets that become the dominant contributors to the electronic Density of States (DOS). Out of these bands, 2 of the hole pockets are quasi-cylindrical and reside at the $\Gamma$ point $(0,0)$ in the folded Brillouin Zone (BZ) (2 Fe-atoms per cell), the 2 overlapping electron pockets reside at the M points $(\pi,\pi)$ and one 3-dimensional hole pocket at the Z point $(0,\pi)$. The 3-dimensional
Figure 2.2: Phase diagram in the Ba122 family. A separate diagram is presented for the 3 main types of doping. Although $T_{\text{N\text{\text{ee}}}l}$ gets reduced quickly with increased doping, the SDW state does not disappear before superconductivity arises, but rather the two seem to coexist over a small doping region. Figure obtained from [12].

hoe pocket, appearing exclusively on the 1111 compounds, seems to be strongly associated with the AntiFM ordering in the material, quickly disappearing with increased doping [20]. Figure 2.3 shows band structure calculations for optimally electron- and hole-doped Ba122 superconductors [22]. Both figures 2.3a and 2.3b show the predicted the central hole pockets and the electron pockets at the corner of the folded BZ.

Angle-Resolved Photoemission Spectroscopy (ARPES) has been used to probe the electronic structure of FeSC’s in their superconductive state, assessing the amplitude and angular variation of the superconductive gap. ARPES has been applied to 1111 and 122 compounds showing fully gapped band structures [23, 24, 25, 26] consistent with the original LDA calculations. Aside from ARPES, heat capacity measurements [16] and London penetration depth measurements [27], which probe the superfluid density and the presence of quasiparticle excitations in the superconductive state of superconductors, have been used to characterize several of the Ba122 compounds. Results from these measurements show fully gapped FS’s for the electron
and hole-doped compounds away from the overdoped regimes, but clear evidence of nodes in the isovalent-doped case and the heavily hole-doped cases. We will return to those special cases in the following section.

A crucial factor that band structure calculations show us is that there is very strong nesting occurring between the hole and electron pockets with a vector $Q = (\pi, \pi)$. This vector is coincidental with the vector $Q_{\text{AF}}$ that characterizes the stripe AntiFM propagation in these materials. One of the possible explanations for this behavior is that the AntiFM ordering is a SDW due to Fermi surface nesting of itinerant electrons rather than local magnetic moments [28], however this theory fails to explain the presence of localized magnetic moments above the structural transition temperature. In light of this, there is the alternate proposal that the AntiFM stripe ordering results from a hybridization of localized moment bands with the bands containing the itinerant electrons [29].

2.2 Pairing symmetry in Fe-based superconductors.

The existence of a superconductive phenomena requires the description of the mechanism through which electrons overcome their natural Coulomb repulsion to form Cooper pairs. BCS stipulated that in conventional superconductivity, the interaction between electrons and the lattice surrounding them, through the exchange of phonons, can create an attractive potential strong enough to form these pairs.

For isotropic superconductive systems, the interaction potential between 2 fermions $U(r)$ can be expanded in components dependent on the angular momentum $l = 0, 1, 2...$ for the fermion pair. If there is a term in the series with an attractive pairing potential the material will undergo a transition at a critical temperature $T_c$. For superconductors described by BCS, most pairing potentials depend on the $l = 0$ term and are thus...
called \textit{s-wave} superconductors\footnote{In analogy with the spatial states outlined by the angular momentum \(l\). There, \(l = 0\) defines the \(s\)-state, \(l = 1\) defines the \(p\)-state, \(l = 2\) defines the \(d\)-state, etc.}. In the same way, cuprates are described by a \textit{d-wave} pairing symmetry. The reason behind it is believed to be that the Coulomb potential in cuprates, \(U(r)\), albeit repulsive at short distance scales, has an attractive component for large \(r\) and higher \(l\).

When the superconductor under analysis is not isotropic but instead described by a particular lattice and its constrictions, rather than using the angular momentum number \(l\) we need to use the symmetry properties of the irreducible space group representation of the lattice in question to describe the material’s pairing symmetry.

For the case of both cuprates and FeSC’s, their superconductive state appears when the materials are in their orthorhombic phase. This lattice structure can be represented by 4 different one-dimensional irreducible space group representations: \(A_{1g}, B_{1g}, B_{2g}\) and \(A_{2g}\) and one two-dimensional representation: \(E_{2g}\). When a superconductive gap appears with a \(A_{1g}\) symmetry, it is usually referred as \textit{s-wave} since the first eigenstate of that representation is a constant in \(k\)-space. Superconductive gaps with \(B_{1g}\) or \(B_{2g}\) symmetry give rise to \textit{d-wave} superconductivity (\(d_{x^2-y^2}\) or \(d_{xy}\)).

When we look at the band structure of FeSC’s and notice the high level of nesting between the low-energy FS pockets near the \(\Gamma\) point in the center of the BZ and the electron pockets at the corners, we realize that the system we are looking for must have translational symmetry under the exchange \(k \rightarrow k + Q\) for \(Q = (\pi, \pi)\); also, it must be invariant under the transformations \(k_x \rightarrow k_y\) and \(k_x \rightarrow -k_x\). The result of these conditions is that the superconductive order parameter must be represented by a small subset of the \(A_{1g}\) symmetry group which receives the name of \textit{extended s-wave} or \(s^\pm\). However, experimental work on FeSC’s point towards a non-trivial pairing symmetry due to the complex interactions between the intraband Coulomb interactions, spin exchange interactions and the momentum structure of the interactions [30]. In particular, the mechanisms that result in a fully gapped \(s^\pm\) structure in weakly/optimally doped FeSC’s can also result in nodal-\(s^\pm\) and \textit{d-wave} at high doping levels.

## 2.2.1 Pairing models candidates for Fe-based superconductors

With the discovery of cuprates, it was evident that electron-phonon interactions were not sufficient to explain the much higher characteristic \(T_c\)’s at which these materials become superconductors. The same situation applies to FeSC’s. Taking an approximation based on the McMillan formalism [31], the calculation of an expected \(T_c\) based solely on electron-phonon interaction for pairing has been proven very accurate when applied to conventional superconductors. However, this approximation has resulted in calculated values for electron-phonon coupling \(\lambda\) and Debye temperature \(\Theta_D\) far away from accepted experimental results, and
predicting $T_c$ of 0K [32]. Similarly, DFT calculations in LaFeAsO$_{1-x}$F$_x$ [33] show that the electron-phonon coupling constant applied to a BCS calculation yielded a predicted $T_c$ of 0.8K, which conflicts with the actual $T_c$ of 45K.

Finally, Wu explains the characteristic isotope effect on FeSC’s [29], which in conventional superconductors, is used to determine the strength of electron-phonon coupling in the Cooper pairing process. This is done by analyzing the dependence of $T_c$ on a change in the lattice constants (and $\Theta_D$) due to the replacement of atoms in the superconductor by isotopes, which have a different mass. Although the previously stated results show the relative irrelevance of electron-phonon coupling in the formation of Cooper pairs, the sizable isotope effect tells us that the value of the lattice constants is important for pairing. This information becomes reconciled with the experimental results when we notice that pressure enhances $T_c$ in FeSC’s, indicating the relevance of the crystal structure in the strength of the superconducting transition in these materials.

The existence of a AntiFM ordered state in all the parent compounds of FeSC’s suggested that the Cooper pairing had to be strongly tied to the exchange of magnetic excitations. Indeed, taking the interaction between itinerant electrons and localized magnetic moments within the FeAs lattice, one can build a model where the conventional phonon pairing described by BCS can be rebuilt using magnons instead of phonons. This type of interactions involve the scattering of an electron pair with momentum ($k, -k$) to another state with momentum ($k', -k'$) with the addition of a spin flip. In terms of an excitation, we can speak of scattering through the exchange of a spin exciton, also known as a magnon.

Given the multiband character of FeSC’s this type of scattering event can happen within bands (hole-hole or electron-electron), also known as intraband interaction, or between different bands (hole-electron), which is called interband interaction. In principle, both processes could produce the necessary conditions for pairing, however, Wu and Phillips notice that through Adler’s theorem, the strength of an interaction mediated by the exchange of a magnon is proportional to the momentum transfer $q = k' - k$. For intraband scattering, each paired electron experiences a momentum transfer of $q$, whereas for interband scattering, the net momentum transfer is $Q + q$. In the limit of small $q$, the intraband contribution to the net interaction vanishes while the interband contribution saturates at a finite value, and thus, dominates the interaction. In figure 2.4, we see a graphic representation of the process of electron scattering from a hole band into an electron band.

However, there is one final missing piece to the puzzle. An interaction between fermions mediated by magnons is always repulsive, unlike the case for phonons. The key in obtaining pairing from an interaction that is always repulsive comes from the multiband nature of the system and the possibility of interband
scattering. By taking an approximation of the system as a two-band model (hole + electron band) [34], we can solve the eigenvalue problem for the hole and electron gaps around all Fermi surfaces:

\[
\lambda \begin{pmatrix} \Delta^h_k \\ \Delta^e_k \end{pmatrix} = -\sum_{k'} \left\langle \begin{pmatrix} V_{hh} & V_{eh} \\ V_{eh} & V_{ee} \end{pmatrix} (k, k') \begin{pmatrix} \Delta^h_{k'} \\ \Delta^e_{k'} \end{pmatrix} \right\rangle_{FS} 
\]

(2.1)

where \(V_{i,j}\) refer to the interaction amplitudes between the different gap types. By defining the dimensionless interaction strengths \(\lambda_e = V_{ee}N_e(E_F)\), \(\lambda_h = V_{hh}N_h(E_F)\) and \(\lambda_{eh} = V_{eh}\sqrt{N_e(E_F)N_h(E_F)}\), where \(N_{\alpha}(E_F)\) correspond to the DOS at the Fermi energy of each of the gaps, we can see that the maximum positive eigenvalue of the equation is:

\[
\lambda = -\frac{(\lambda_h + \lambda_e)}{2} + \sqrt{\frac{(\lambda_h - \lambda_e)^2}{4} + \lambda_{eh}^2} 
\]

(2.2)

with the corresponding eigenstates:

\[
\begin{pmatrix} \Delta^h_k \\ \Delta^e_k \end{pmatrix} \propto \begin{pmatrix} \lambda_{eh} \\ -\lambda_h \end{pmatrix} 
\]

(2.3)

With the condition that \(\lambda > 0\), we see that \(\Delta^h_k\) and \(\Delta^e_k\) will have a different sign if \(\lambda_{eh} > 0\). It is this last statement that completes the definition of \(s\pm\) pairing: the formation of Cooper pairs through the interband interaction between electrons through the exchange of a magnon, given that the order parameter of the hole

Figure 2.4: Possible interband scattering events for Cooper pairing.
pockets on the Fermi surface have a phase shift of $\pi$ respect to the order parameter of the electron pockets.

So far, although the $s\pm$ model adjusts itself very well to the collection of experimental results obtained over the years regarding the properties of FeSC’s, a definitive confirmation remains elusive. So far, the strongest evidence supporting its validity comes from inelastic neutron scattering experiments [35, 36, 37]. In these measurements, a strong resonance has been detected for a vector $\mathbf{Q} = (\pi, \pi)$ which is coincidental to the vector connecting the hole and electron pockets in the FS. If the resonance is due to spin excitations, it can only happen for electron and hole pockets having opposite signs, as explained in this section.

It is worth considering that the case of superconductivity in cuprates has a strong similarity with that of FeSC’s in that their pairing is also believed to be mediated by the exchange of spin fluctuations. By looking at the band structure in cuprates, we can see that a strong nesting condition can also be found with $\mathbf{Q} = (\pi, \pi)$, but this time, the difference resides in that cuprates are single-band superconductors, so $\mathbf{Q}$ connects different parts of the same Fermi surface. Again, since the spin fluctuations are interactions that remain repulsive, the different sections of the cuprate superconductor’s order parameter connected by $\mathbf{Q}$ must have opposite signs, and the result of this condition is $d$-wave superconductivity. Finally, just as with FeSC’s, inelastic neutron scattering also finds a resonance with $\mathbf{Q} = (\pi, \pi)$, which was seen as one of the signatures of this type of pairing.

### 2.2.2 Alternatives and variations to the $s\pm$ model.

The analysis presented in section 2.2 was done considering that the hole and electron pockets in FeSC’s Fermi surfaces are individually isotropic, albeit distributed along different zones in the BZ. However, band structure calculations have shown that the gaps are not perfectly cylindrical but rather have angle-dependent perturbations. In particular, we can fit the amplitude of the electron gap to $\Delta_e(k) = \Delta_e \pm \tilde{\Delta}_e \cos 2\phi_k$. This oscillation in the gap amplitude can usually be considered small, but there could be cases in which these oscillations are large, leading to a nodal $s$-wave structure or even a sign-change electron gap. In the $s\pm$ model there are no restrictions towards these conditions, since even with an electron gap with alternating sign, as long as the average sign around the pocket remains opposite to that of the hole gap, the pairing mechanism remains the same. Thus several interesting cases can be described in the subject of pairing in FeSC’s based on the same $s\pm$ model. To appreciate the comparison between different pairing symmetry models, refer to the representations of each of the most common ones in figure 2.5. We will discuss a few examples of alternatives to the isotropic $s\pm$ model, specifically the effects of doping, and the evidence supporting them.

While the scientific consensus favors the use of the $s\pm$ model to explain the pairing in FeSC’s, there are still proponents of other models, like the $s++$ model seen in MgB$_2$, arguing that some of the data used to
support s± can also be used to favor of s++, depending on the interpretation. In general, since s± and s++ are models that arise from the same point group symmetry, the discussion about the differences between them boils down to whether the sign of the electron and hole gaps is different or equal. In particular, proponents of s++ [39] argue that the resonance seen by inelastic neutron scattering is not as sharp as the one seen in cuprates and it is unclear that it appears below an energy of 2Δ for the smallest gap in the FeSC. Supporters of s± argue that the broader peak in the neutron scattering data is due to the cos 2φ component in the amplitude of the electron gap.

Another interesting example of variations in s± superconductivity across families of FeSC’s is the one presented by the isovalently-doped compounds. For these materials, where P is used to substitute As atoms, there is strong evidence of nodal s± superconductivity in all of the families. ARPES, London penetration depth and heat capacity measurements [40, 41, 42] have shown clear evidence of line nodes in these materials, yet although many explanations have been offered for this phenomenon, no consensus has been achieved yet.

Finally, for the case of strongly hole doped Ba122, the limiting case offered by KFeAs is extremely interesting because it deviates from the s-wave pairing into the d-wave regime. In particular, ARPES data [43] has shown the disappearance of the electron pockets at the M points in the BZ in favor of hole blades that don’t favor nesting. Thus, the system has only the hole pockets at the Γ point in the BZ, out of which,
one of them shows evidence of nodes due to a strong $\cos 4\phi$ component in the gap amplitude. Whether this nodes are due to $d$-wave pairing or to nodal $s$-wave superconductivity is not yet clear and remains a controversial issue.
Chapter 3

Theoretical background

In this chapter, we cover the background and predictions regarding the characterization of the pairing symmetry of Fe-based superconductors through two main avenues. Our first approach is through the behavior of Josephson junctions where the Fe-based superconductor (FeSC) is linked to a conventional superconductor through a normal metal weak link (SNS± Josephson junctions) and the analysis of the effects of changes in the junction geometry and the presence of magnetic flux on the characteristic properties of the heterostructure. This type of measurement is known as Josephson interferometry and the transport properties measured through this approach are determined by Cooper pairs directly tunneling into the FeSC.

The second approach is dependent not on a direct tunneling effect as in Josephson interferometry, but rather on the proximity-induced changes in the density of states (DOS) of a conventional superconductor because of a link to a FeSC by a weak barrier. In this case, the characterization of the pairing symmetry is done through the analysis of the DOS spectrum of the conventional superconductor, which can be done through several established tunneling techniques.

Thus we will begin exploring the fundamentals of each of the two chosen experimental designs, followed by their application to the pairing symmetry problem and the specific predictions regarding the Ba122 superconductor system.

3.1 Josephson Interferometry

3.1.1 Development and Principle of operation

The experimentally confirmed Josephson effect was predicted in 1962 by B. D. Josephson [44]. Although it was originally described as a characteristic phenomenon of tunnel junctions, it turns out that this effect applies to a much wider family of superconductor structures. The necessary element for the Josephson effect to occur is the presence of a weak link between two superconductors. This link must be able to carry a supercurrent, but not have the strong superconducting properties of the materials it is connecting. In more specific terms, if a material is linking 2 superconductors α and β, it will be considered a weak link if, for
a change in the superfluid phase $\phi_\beta$ of superconductor $\beta$ by a total of $2\pi$, the link is left without a phase gradient and, thus, comes reversibly to the original state in which it started.

Given this condition, we start the analysis of this superconductor arrangement by representing the free energy $F$ as a periodic function of the phase difference $\phi = \phi_\alpha - \phi_\beta$. This relationship can generally be represented through the following expression:

$$F = -F_0 \cos \phi \quad \text{for } |F_0| > 0 \quad (3.1)$$

As a consequence of this relation, $F$ is minimized when $\phi = 0$. This condition can be expanded through the London formalism by taking the familiar relationship:

$$\hbar \frac{\partial \phi}{\partial t} = -2e(\mu_\alpha - \mu_\beta) = 2eV, \quad \text{where } V = \mu_\beta - \mu_\alpha \quad (3.2)$$

for $V$ representing the voltage across the weak link. After inserting this expression back into equation 3.1 we notice that a slow increase in $\phi$ by means of a small voltage across the link simplifies the differentiation of equation 3.1 yielding:

$$\frac{dF}{dt} = I_s V = \frac{\partial F}{\partial \phi} \frac{d\phi}{dt} = F_0 \sin \phi \frac{2eV}{\hbar}$$

$$I_s = I_J \sin \phi \quad (3.3)$$

where $I_J = 2eF_0/\hbar$ receives the name of Josephson critical current, and $I_s$ is defined as the supercurrent flowing through the link. When superconductors $\alpha$ and $\beta$ are linked through 2 weak links –forming 2 Josephson junctions 1 & 2– in the presence of a magnetic field $B$, we can see that by comparing the individual phase differences for the 2 individual Josephson junctions, $\phi_1$ and $\phi_2$, their difference must be a multiple of $2\pi$, or else a supercurrent would flow along the closed path between the superconductors. This argument favors a quantization condition for the the magnetic flux $\Phi$ in the area between the two Josephson junctions. The resulting condition is that the phase difference $\phi_1 - \phi_2 = 2\pi$ when the flux through the enclosed area is a multiple of a flux quantum $\Phi_0 = h/2e$:

$$\phi_1 - \phi_2 = 2\pi \frac{\Phi}{\Phi_0} \quad (3.4)$$

This relationship reminds us of the expression for the interference pattern between 2 beams of light. It follows that the critical current $I_c$ of this arrangement, as a function of $\Phi$ follows the same profile as the
intensity of a diffraction pattern for light coming out of two thin slits. For the case of 2 identical Josephson junctions, the value of $I_c$ as a function of $\Phi$ is given by:

$$ I_c = 2 I_J \left| \cos \left( \frac{\pi \Phi}{\Phi_0} \right) \right| $$  \hspace{1cm} (3.5)

which has the familiar shape we can see in figure 3.2. This arrangement of Josephson junctions is called Superconductive Quantum Interference Device, or SQUID. As it will be seen later, when the 2 junctions in a SQUID arrangement are not equal –junctions with different characteristic $I_c$’s or geometries–, the patterns that are created deviate respect to the one shown in equation 3.5, thus shining light on the particular properties of the involved Josephson junctions.

Figure 3.1: Diagram of a single Josephson junction with a magnetic field $B$ perpendicular to its axis. In this diagram, the weak link is described as a barrier of thickness $t$ connecting superconductors $\alpha$ and $\beta$. Due to the penetration of the magnetic field $B$ into each of the superconductors as far as their London penetration depths, $\lambda_\alpha$ and $\lambda_\beta$ respectively, the effective length of the Josephson junction is determined by $L = t + \lambda_\alpha + \lambda_\beta$. The total area of the junction perpendicular to the junction is determined by $A_J = L \cdot x$.

Quantum interference modulated by the presence of magnetic flux is also seen in single Josephson junctions. Considering a junction lying in the x-z plane with a magnetic field $B$ perpendicular to the axis of the structure, we take a loop that crosses the junction in points 0 and $x$ in the x-axis. See figure 3.1. Taking the phase difference in the edge of the junction as $\phi_0 = \phi(x = 0)$ and considering equation 3.4, then, the phase difference at point $x$, $\phi(x)$, would be:

$$ \phi(x) = \phi(0) - 2\pi \frac{\Phi(x)}{\Phi_0} $$

$$ = \phi(0) - 2\pi \frac{B A_J(x)}{\Phi_0} $$

$$ = \phi(0) - 2\pi \frac{B x L}{\Phi_0} $$  \hspace{1cm} (3.7)

for $A_J(x)$ being the area of the junction at $x=x$. This is also analogous to the representation of the diffraction
condition for light going through a thin single slit. Taking a Josephson junction of dimension $c$ in the $y$-axis and total width $2 \cdot a$, the total critical current, taken from equation 3.3, can be represented as:

$$I_c = \int_{-a}^{a} c J_J \sin(\phi(x)) \, dx$$  \hspace{1cm} (3.8)$$

$$I_c = ac J_J \left| \frac{\sin(\pi B a L/\Phi_0)}{\pi B a L/\Phi_0} \right|$$  \hspace{1cm} (3.9)$$

for $J_J$ being the Josephson critical current density. This equation shows how an applied magnetic flux modulates the maximum critical current circulating through a single Josephson junction. A diagram of $I_c$ vs $\Phi$ can be seen in figure 3.2. This type of pattern shall be referred to, from now on, as a Fraunhofer pattern in analogy to the single slit light interference pattern. As stated in section 4.1.2, Josephson junctions can be fabricated in different geometries depending on the material and the particular purpose of the structure. These structures favor tunneling, in principle, only in one $k$ with direction parallel to the area vector of the surface on which they are fabricated. Thus, uniform junctions fabricated on flat surfaces (what we define as edges) would modulate with an applied magnetic field $B$ according the relation in equation 3.9, however, for a Josephson junction spanning several different flat surfaces at particular angles, the integral in equation 3.8 must be split in parts representing the junctions on both sides of the particular geometry. In this splitting, the individual integrals may not be identical since the maximum $J_J$ for different geometries can be strongly dependent on the specific set of $k$ probed by the fabricated junctions, thus, each numerical contribution depends on the particular tunneling properties of the surface under analysis.

It is worth noting that, going back to equation 3.3 for the magnitude of the supercurrent $I_s$ circulating through a Josephson junction, we can take the one-dimensional Ginzburg-Landau equation and solve for the maximum critical current $I_c$ (see [45]). For the specific case of a short junction (defined by $\xi/d \gg 1$), we can arrive at the following expression:
\[ I_s = I_c \sin \phi \]  
(3.10)

where \( I_c = \frac{2e\hbar \Phi^2_\infty}{m^* A J} \)  
(3.11)

where \( \Phi^2_\infty \) is the GL spatial order parameter evaluated at infinity. We can see that \( I_c \) scales inversely with the normal state resistance of the material \( R_N = \rho_N \frac{d}{A J} \), such that the product \( I_c R_N \) has the form:

\[ I_c R_N = \frac{2e\hbar \rho_n \Phi^2_\infty}{m^*} \]  
(3.12)

Equation 3.12 shows us that the product \( I_c R_n \) is not dependent on the geometry of the Josephson junction, but only on the temperature and the properties of the materials used in the fabrication of the junction. For the case of a tunnel junction, Ambegaokar and Baratoff [46] derived the exact result which has the form:

\[ I_c R_n = \frac{\pi \Delta^2}{2e} \tanh \frac{\Delta}{2kT} \]  
(3.13)

which only depends on the temperature and the value of the superconducting gap \( \Delta \). This result is general and is valid for a normal metal link in the vicinity of \( T_c \). For our purposes, we will use this result to characterize junctions with different effective superconducting gaps.

### 3.1.2 Josephson Interferometry probing anisotropic order parameters

As we can see from equations 3.8 and 3.9, the Fraunhofer pattern seen in the \( I_c \Phi \) curves in figure 3.2a only occurs when \( J_J \) is isotropic in magnitude and phase along the complete width of the Josephson junction. The power of Josephson interferometry as a tool to elucidate the symmetry in the pairing mechanism of unconventional superconductors comes from the identification of the variations in the shape of the \( I_c \Phi \) curves due to the anisotropy of the order parameter in these superconductors.

In a Josephson junction with a conventional (s-wave) and an unconventional superconductor, \( J_J \) is dependent on the magnitude of the superconducting order parameter of both materials, \( \Delta_s \) and \( \Delta_{unc} \) respectively, and their phases, \( \phi_s \) and \( \phi_{unc} \). For the simple case of constant \( \Delta_{unc} \), \( \phi_{unc} = \Delta_{unc,0} \), \( \phi_{unc,0} \), we recover equation 3.9. Otherwise, for the case where these quantities are \( k \)-dependent, \( \Delta_{unc} = \Delta_{unc}(k) \) and \( \phi_{unc} = \phi_{unc}(k) \) and, thus, could exhibit a spatial variation within the geometry of the Josephson junction, instead of using equation 3.9, we must go back to the following general expression:
Figure 3.3: Josephson interferometry applied to junctions with anisotropic order parameters. Figure 3.3a refers to the signature of d-wave superconductivity as seen by the double central lobes. A phase difference of $\pi$ between sections of the junction creates this pattern. Figure 3.3b refers to a general case where there is an anisotropic value of $\Delta$ but no phase difference of $\pi$ between sections of the junction. On both cases, the dotted line shows a regular Fraunhofer pattern.

\[ I_c = \int_{-a}^{a} c \, J_j(x) \sin \phi(x) \, dx \]  \hspace{1cm} (3.14)

where $J_j$ is a function of the coordinate $x$ which runs perpendicular to the junction axis. Taking this relation, we can identify 2 cases of interest in our experimental setup:

1. **Sign-changing order parameter**: In this case, a phase change $\delta \phi \geq \pi$ between 2 points in the overall unconventional order parameter probed by the Josephson junction will transform the Fraunhofer pattern seen in figure 3.2a into a double peak pattern seen in figure 3.3a. This characteristic change in the $I_c \Phi$ curves can be used as a signature of d-wave pairing symmetries like the work done on cuprate superconductors.

2. **Magnitude-changing order parameter**: For this case, the Josephson junction will have an uneven $J_c$ across its area but no sign change in the order parameter. The resulting $I_c \Phi$ curve will still have a central peak but the value of $I_c$ will not reach zero after 1 flux quantum $\Phi_0$ but only a local minimum. This side-lobe lifting can be seen in figure 3.3b.

As seen in section 2.2, the $s\pm$ pairing model linked to FeSC requires the definition of a phase difference of $\pi$ between hole-like pockets the electron-like pockets in the folded Brillouin zone (BZ). Starting form the center of the BZ, we can take different $\mathbf{k}$ that span the whole $k_x - k_y$ plane\(^1\). As we move around the center of the BZ, we notice that a set of $\mathbf{k}$ crosses only the hole pockets while a smaller set of $\mathbf{k}$ includes both hole and electron pockets.

Wu and Phillips [47] proposed a way of probing the phase anisotropy in FeSC crystals with the aid of a SQUID devices fabricated along two adjacent facets. The proposed geometry can be seen in figure 3.4a.

\(^1\)We take the limit where the pockets in the Fermi surface are cylindrical, thus they don’t offer a surface in the $k_z$ direction. In reality, there is a defined Fermi surface in the $k_z$ direction, albeit much smaller than in the $k_x - k_y$ plane.
Facets on the crystal surface perpendicular to the a-b plane would be selected such that one would be aligned with the a- or b-axis of the crystal and the other describes an angle of 45°, 135°, 225° or 315° respect to the first one. The angle between the facets is chosen such that a Josephson junction fabricated on a surface parallel to the a- or b- axis will have Cooper pairs with \( k \) circa \((\pm 1, 0)\) or \((0, \pm 1)\) tunneling into the FeSC, which correspond to tunneling directions that only intercept the hole pockets in the center of the folded BZ. In the same way, a Josephson junction built on the angled face will have Cooper pairs with \( k \) circa \((\pm 1, \pm 1)\) or \((\pm 1, \pm 1)\) entering the FeSC, corresponding to tunneling directions that intercept both hole pockets in the center of the BZ and both electron pockets at the M point of the folded BZ.

Due to the difficulty of tuning the fabrication of SQUIDs on polished crystal surfaces, a variation of that experimental setup was developed using the same crystal geometry but with single Josephson junctions instead of SQUIDs. This altered geometry can be seen in figure 3.4b. The difference between this approach and the proposed SQUID interferometry resides on the fact that a single junction can probe both facets on the crystal simultaneously by the creation of a *corner junction*. For this geometry, we would be probing the change in the unconventional order parameter of the FeSC between the two crystal faces that the Josephson junction is characterizing.

This corner junction arrangement has been successfully used in the past to identify the sign-changing order parameter in cuprate superconductors [48, 49] and in the heavy fermion superconductor UPt3 [50]. Thus, it serves us well as a first approach study of pairing symmetry in new superconductors. However, for the case of FeSC’s there is a feature in the interpretation of the results that can be problematic if the fabrication of Josephson junctions cannot be made into a highly repeatable and consistent fashion. This issue arises by noticing that patterns seen in figure 3.3b characterize single-junction Josephson interferometry measurements when there is an anisotropic, but not sign-changing, order parameter across the width of the
fabricated device. For the experimental case portrayed in figure 3.4b, two competing pairing symmetry models, the s++ and the s±, offer each a possible scenario that results in almost identical interference patterns:

- For the s± model, a corner junction probes two sets of \( k \); the first set interacts only with the central hole pockets in the BZ characterized by an isotropic gap \( \Delta_0 \), whereas the second set interacts with both the hole pockets and the electron pockets (characterized with a quasi-isotropic gap \( \Delta_1 = -|\Delta_1| \)). The effect of the combination of the two types of gaps can be described by an effective gap \( \Delta_{eff} \) such that \( 0 < \Delta_{eff} < \Delta_0 \).
- For the s++ model, a corner junction probes two sets of \( k \); the first set interacts only with the central hole pockets in the BZ characterized by an isotropic gap \( \Delta_0 \), whereas the second set interacts with both the hole pockets and the electron pockets (characterized with a quasi-isotropic gap \( \Delta_1 = +|\Delta_1| \)). The effect of the combination of the two types of gaps can be described by an effective gap \( \Delta_{eff} \) such that \( \Delta_0 < \Delta_{eff} \).

The result of a Josephson interferometry experiment on Ba122 crystals with either of these characteristic pairing models can be seen in figure 3.5. For both cases the same core elements persist: a maximum for \( I_{c,max} = I_c(\Phi = 0) \), elevated side lobes and the first global minimum at \( I_{c,min} = I_c(\Phi = 2\Phi_0) \). However, we notice that when these patterns are compared with a regular Fraunhofer pattern from a junction probing an isotropic superconductive gap \( \Delta_0 \) such that \( I_{c,0} = I_c(\Phi = 0) \), the s± case yields the condition \( I_{c,max} < I_{c,0} \) (see figure 3.5a), whereas the s++ case yields the condition \( I_{c,max} > I_{c,0} \) (see figure 3.5b). Thus, a reference device made on a flat crystal facet probing only the central hole pockets in the BZ (see again figure 3.4b), with identical junction area and barrier type and thickness is necessary to discriminate between extended-s pairing symmetry models. To circumvent the complications of this requirement, we use the \( I_c R_N \) product in combination with the Josephson interferometry results to account for variations in junction area and barrier thickness as long as the nature of the barrier remains constant.
3.2 Proximity-induced signatures of $s\pm$ superconductivity

In this chapter, we present a scenario regarding the proximity coupling of a conventional $s$-wave superconductor with a multiband superconductor, such as the case with FeSC’s, where the $s\pm$ model might be applied to explain its pairing mechanism. This formalism was presented by Alexei Koshelev and Valentin Stanev [51] and offers a different way to obtain confirmation of the adequacy of the $s\pm$ model to explain the superconductive state in FeSC’s. The difference between this prediction and previous experimental proposals lies in that, although several experimental implementations of the Josephson effect as a phase sensitive tool have been documented for the FeSC systems (see [52, 53, 54, 47, 55]), these experiments require electrical transport in very restricted conditions and geometries, which has been proven very difficult. Nevertheless, Koshelev and Stanev propose an indirect measurement where the Josephson effect serves as a way of linking a conventional superconductor with the proposed $s\pm$ but where no special directional tunneling is required, relaxing the conditions under which the measurement can be carried out.

3.2.1 Proximity coupling between a conventional superconductor and an $s\pm$ superconductor

For this microscopic analysis, Koshelev and Stanev use the Usadel equations generalized to a multiband superconductor for the case in which a thin layer of a conventional $s$-wave superconductor (its thickness $d_s \ll \xi_s$, where $\xi_s$ is the superconductive coherence length) is put in weak contact with a multiband $s\pm$ superconductor (taken in the case of only 2 gaps), both of them in the dirty limit. This arrangement in itself forms a Josephson junction, but rather than worrying about its transport properties, we instead look at the effect the $s\pm$ superconductor produces in the $s$-wave.

For the thin $s$-wave superconductor existing in a region between $0 < x < d_s$, one can write the Green’s function $\Phi_s$ such that:
\[
\frac{D_s}{2\omega G_s} \left[ G_s^2 \Phi'_s \right]' - \Phi_s = -\Delta_s, \quad G_s = \frac{\omega}{\sqrt{\omega^2 + \Phi_s^2}}
\]  

(3.15)

where here \(D_s\) refers to the diffusion coefficient in the \(s\)-wave superconductor (related to the conductivity \(\sigma_s\) by \(\sigma_s = e^2 \nu_s D_s\), where \(\nu_s\) is the normal state DOS) and \(\omega = 2\pi T(n + 1/2)\) refers to the Matsubara frequencies. When looking at the boundary conditions, at \(x = d_s\), we have \(\Phi'_s = 0\), however, for the boundary between \(s\) and \(s\pm\), we turn to Brinkman’s analysis of Usadel equations for multiband systems [56]. In this region we see the following boundary conditions:

\[
\xi_s G_s^2 \Phi_s = \sum_{\alpha} \frac{\xi_{\alpha}}{\gamma_{\alpha}} G_{\alpha}^2 \Phi'_\alpha, \quad \text{with} \quad \gamma_{\alpha} = \frac{\rho_{\alpha} \xi_{\alpha}}{\rho_s \xi_s},
\]

(3.16)

\[
\gamma_{Ba} \xi_s G_s \Phi'_s = G_s (\Phi_s - \Phi_\alpha), \quad \text{with} \quad \gamma_{Ba} = \frac{R_{B\alpha}}{\rho_{s\alpha} \xi_s}.
\]

(3.17)

where \(\rho_{s(\alpha)}\) refers to the resistivity of the \(s(s\pm)\) superconductor, \(\alpha = 1, 2\) indicating each of the 2 gaps considered for the \(s\pm\) superconductor, \(R_{B\alpha}\) refers to the partial resistances at the boundary between the \(s\) and \(s\pm\) superconductors which determine the electrical coupling between the two. For the case of weak coupling, we can approximate the Green’s functions \(\Phi_s, \alpha\) as \(\Phi_s \approx \Delta_s\) and \(\Phi_\alpha \approx \Delta_\alpha\) given that \(\gamma_{Ba} \gg 1\), so the approximate boundary conditions can be expressed as:

\[
\xi_s G_s \Phi'_s = \sum_{\alpha} \frac{G_{\alpha}}{\gamma_{Ba}} (\Delta_s - \Delta_\alpha), \quad \text{with} \quad \gamma_{Ba} = \gamma_{\alpha} \gamma_{Ba} = \frac{R_{B\alpha}}{\rho_{s\alpha} \xi_s}.
\]

(3.18)

It is worth considering that while \(\gamma_{1,2}\) refer to properties of the bulk of the material, \(\gamma_{B(1,2)}\) refer to properties of the interface only. Taking the Green’s function in equation 3.15 with the boundary condition in equation 3.18, we can construct the correction to the Green’s function of the \(s\)-wave superconductor because of the proximity effect of the \(s\pm\) superconductor. Taking the case where \(d_s \ll \xi_s\), we can expand the Green’s function as follows:

\[
\Phi_s(x) \approx \bar{\Phi}_s + a_s \frac{\alpha_s}{2} (x - d_s)^2
\]

(3.19)

which, when applied to equation 3.15, results in:

\[
\frac{D_s}{2\omega} G_s a_s \approx \bar{\Phi}_s - \bar{\Delta}_s
\]

(3.20)

Taking equation 3.18 and using the approximation in equation 3.19, we can match the boundary condition
at \( x = 0 \) as follows:

\[
x_{s} G_{s} a_{s} d_{s} = - \sum_{\alpha} \frac{G_{\alpha}}{\gamma_{B\alpha}} (\Delta_{s} - \Delta_{\alpha})
\] (3.21)

Solving equations 3.20 and 3.21 results in:

\[
\Phi_{s} - \Delta_{s} \approx - \sum_{\alpha} \frac{\Gamma_{s,\alpha} (\Delta_{s} - \Delta_{\alpha})}{\gamma_{B\alpha}}
\] (3.22)

where:

\[
\Gamma_{s,\alpha} \equiv \frac{D_{s}}{2 \xi_{s} d_{s} \gamma_{B\alpha}} = \frac{\rho_{s} D_{s}}{2 d_{s} R_{B}^{\alpha}} = \frac{1}{2 e^{2} \nu R_{B}^{\alpha} d_{s}}
\] (3.23)

considering that \( \Gamma_{s,\alpha} \) is introduced as the coupling parameter between the \( s \)-wave superconductor and each of the bands in the \( s \pm \) superconductor. Now, we take equation 3.22 and apply an analytical continuation into real energies \( i\omega \rightarrow E - i\delta \), resulting in:

\[
\Phi_{s} \approx \Delta_{s} + \sum_{\alpha} \frac{\Gamma_{s,\alpha} (\Delta_{\alpha} - \Delta_{s})}{\sqrt{\Delta_{\alpha}^{2} - E^{2}}}
\] (3.24)

which, when combined with:

\[
N_{s}(E) = \Re \left[ \frac{E}{\sqrt{E^{2} - \Phi_{s}^{2}}} \right]
\] (3.25)

results, after expanding the terms, in:

\[
N_{s}(E) = \Re \left[ \frac{E}{\sqrt{E^{2} - \Delta_{s}^{2}}} + \frac{E \Delta_{s}}{(E^{2} - \Delta_{s}^{2})^{3/2}} \sum_{\alpha} \frac{\Gamma_{s,\alpha} (\Delta_{\alpha} - \Delta_{s})}{\sqrt{\Delta_{\alpha}^{2} - E^{2}}} \right].
\] (3.26)

Taking the result in equation 3.26 we start introducing the assumptions about our system. Considering the \( s \pm \) system as a 2-band superconductor where the superconductive gaps \( \Delta_{1} \) and \( \Delta_{2} \) have a phase difference of \( \pi \), or in other words, have opposite signs, we state that \( |\Delta_{1}| > |\Delta_{2}| > |\Delta_{s}| \), \( \Delta_{1} > 0 \) and \( \Delta_{2} = -|\Delta_{2}| < 0 \), considering in this case that \( \Delta_{s} > 0 \). These assumptions represent a system where the phase of the \( s \)-wave superconductor will align itself with the phase of one of the 2 gaps in the \( s \pm \) superconductor and anti-align itself with the other gap. The result, as seen in figure 3.6, is a series of perturbations to the DOS spectrum of the \( s \)-wave superconductor, showing features at energies coincidental to the \( s \pm \) gap energies. The type of feature (peaks or dips) in the DOS spectrum refers to the relative phase between \( \Delta_{s} \) and the particular gap \( \Delta_{1,2} \), where a peak signifies alignment and a dip represents anti-alignment between the gaps. The presence of the former of the features is not surprising, however it is the latter feature, the dip in the DOS, which creates a signature pattern exclusive to \( s \pm \) superconductors.
Figure 3.6: Perturbation in the DOS of a thin $s$-wave superconductor in proximity with an $s\pm$ superconductor. We can see the DOS of a superconductive $s$-wave film (dotted line) and how the alignment and anti-alignment of the $s$-wave gap with the gaps of the $s\pm$ superconductor creates enhancements and decreases in the DOS of Al at energies $E = \Delta_\alpha$. It is the presence of these two types of features (peaks and dips in the DOS) that constitutes the signature of $s\pm$ superconductivity. Figure taken from [51].

Taking equation 3.26, we can calculate the relative change in the DOS the $s$-wave superconductor, giving us the following expression:

$$\delta N_s(E) = \frac{E\Delta_s}{(E^2 - \Delta_s^2)^{3/2}} \left[ \frac{\Gamma_{s,1} (\Delta_1 - \Delta_s)}{\sqrt{\Delta_1^2 - E^2}} \Theta(\Delta_1 - E) - \frac{\Gamma_{s,2} (|\Delta_2| + \Delta_s)}{\sqrt{\Delta_2^2 - E^2}} \Theta(|\Delta_2| - E) \right]$$  

(3.27)

where $\Theta(x)$ is the step function. Equation 3.27 shows us that the amplitude of the corrections to the DOS are proportional to $\Delta_1 - \Delta_s$ and $|\Delta_2| + \Delta_s$.

### 3.2.2 Frustrated case in proximity coupling between a conventional and an $s\pm$ superconductor

The analysis presented in section 3.2.1 refers to a proximity-favored state in which the DOS of an $s$-wave superconductor experiences an enhancement or a frustration because of the coupling of its gap to the gaps of an $s\pm$ superconductor. However, Stanev and Koshelev [57] show that this state, called and aligned state arises only when a very particular combination of the coupling constants $\gamma_{B(1,2)}$ is achieved, mediating the strength of the link between $\Delta_s$ and $\Delta_{1,2}$. Moreover, depending on the ratio of $\gamma_{B,1}/\gamma_{B,2}$, a negative proximity effect can be detected as a suppression of $\Delta_s$ and even a frustrated state where there is an overall suppression of all gaps at the interface and a finite phase difference between $\Delta_s$ and $\Delta_{1,2}$ is presented. For this particular coupling regime, we see a state that breaks time reversal symmetry, and the overall gap
suppression may harmfully affect the possibility of a clear measurement.

To better see these effects, we can start with the analysis performed for the $s$-wave superconductor and add the Green’s formalism applied to the $s\pm$ superconductor. Starting with the Usadel equations, as in equation 3.15 but applied to the multiband superconductor, we can write the Green’s function as following:

\[ D_\alpha \frac{G_\alpha^2 \Phi'_\alpha}{2\omega} - \Phi_\alpha = -\Delta_\alpha \]  
\[ 2\pi T \sum_{\beta,\omega>0} \lambda_{\alpha\beta} \frac{G_\beta \Phi_\beta}{\omega} = \Delta_\alpha, \quad G_\alpha = \frac{\omega}{\sqrt{\omega^2 + |\Phi_\alpha|^2}} \]  

where $G_\alpha$ and $\Phi_\alpha$ denote the Green’s functions applied to both bands ($\alpha = 1, 2$) in the $s\pm$ superconductor. $D_\alpha$ denotes the diffusion coefficients (related to $\sigma_\alpha$) and in order to normalize the energy scales, $T^c_s$ and $T^c_\pm$, the critical temperatures for the $s$ and the $s\pm$ superconductors respectively, are introduced. Thus, we can redefine the coherence lengths as $\xi_\alpha = \sqrt{D_\alpha/2\pi T^c_\pm}$ and $\xi^*_s = \sqrt{D_s/2\pi T^c_\pm} = \xi_s \sqrt{T^c_s/T^c_\pm}$. Now, taking the boundary conditions at $x = 0$ as seen in equation 3.18, we construct the expression considering now the $s\pm$ superconductor:

\[ \xi^*_s G_s \Phi'_s = \sum_{\alpha} \xi_\alpha \frac{G_\alpha^2 \Phi'_\alpha}{\gamma_\alpha}, \quad \gamma_\alpha = \frac{\rho_\alpha \xi_\alpha}{\rho_s \xi^*_s} \]  
\[ \xi_\alpha G_\alpha \Phi'_\alpha = -\frac{1}{\gamma_{Ba}} G_s (\Phi_\alpha - \Phi_s), \quad \gamma_{Ba} = \frac{R_{Ba}}{\xi_\alpha \rho_\alpha} \]  

which, when combined, result in:

\[ \xi^*_s G_s \Phi'_s = \sum_{\alpha} \frac{1}{\gamma_{Ba}} G_\alpha (\Phi_\alpha - \Phi_s) \]  

where $\gamma_{Ba}$ keeps the same definition as in equation 3.17 and $\gamma_{Ba} = \gamma_{Ba} \gamma_\alpha$. Performing again an analytical continuation to real energies $i\omega \rightarrow E - i\delta$, the normalized DOS expression for both $s$-wave and $s\pm$ superconductors is:

\[ N_{s,\alpha}(E, x) = \Re \left[ G_{s,\alpha}(E, x) \right] = \Re \left[ \frac{E}{\sqrt{E^2 - \Phi_{s,\alpha}(E, x)\Phi^*_{s,\alpha}(-E, x)}} \right]. \]  

For the case of weak coupling between the superconductors (where $\gamma_{Ba} \gg 1$), the proximity-induced changes in the Green’s functions and the gaps are small and can be treated as small perturbations such
that \( \Delta_{s,\alpha}(x) = \Delta_{s,\alpha,0} + \tilde{\Delta}_{s,\alpha}(x) \) and \( \Phi_{s,\alpha}(x) = \Delta_{s,\alpha,0} + \tilde{\Phi}_{s,\alpha}(x) \). The corrections \( \tilde{\Phi}_{s,\alpha}(x) \) and \( \tilde{\Delta}_{s,\alpha}(x) \) can be computed analytically in the linear order with respect to \( 1/\gamma_{B\alpha} \) (see [57], Appendix A). Since we are looking at the effect of the \( s\pm \) superconductor on the thin \( s \)-wave film, the sign of \( \tilde{\Delta}_{s,0} \), which represents the correction to the \( s \)-wave gap parameter because of the contact to the \( s\pm \) superconductor, tells us whether the \( s \)-wave superconductor has experienced a positive or negative proximity effect (enhancement or suppression of the superconductivity). An analytical expression of the normalized average gap correction can be seen as:

\[
\frac{\tilde{\Delta}_{s,0}}{\pi T_c^{\pm}} = \xi_s^{\pm} \sum_{\alpha} U\left( \frac{\Delta_{s,0}}{|\Delta_{\alpha,0}|} \right) \frac{\Delta_{\alpha,0} - \Delta_{s,0}}{\gamma_{B\alpha}|\Delta_{\alpha,0}|},
\]

with \( U(a) = \frac{K(1-a^2) - E(1-a^2)}{1-a^2} \) (3.34)

where \( K(m) = \int_0^{\pi/2} (1 - m \sin^2(\theta))^{-1/2} d\theta \) and \( E(m) = \int_0^{\pi/2} (1 - m \sin^2(\theta))^{1/2} d\theta \) are the complete elliptical integrals. For the particular case \( \Delta_{s,0} \ll |\Delta_{\alpha,0}| \), equation 3.34 can be approximated as:

\[
\frac{\tilde{\Delta}_{s,0}}{\pi T_c^{\pm}} \approx \xi_s^{\pm} \sum_{\alpha} \frac{\Delta_{\alpha,0} - \Delta_{s,0}}{\gamma_{B\alpha}|\Delta_{\alpha,0}|} \left[ \ln \left( \frac{4|\Delta_{\alpha,0}|}{\Delta_{s,0}} - 1 \right) \right]
\]

Equation 3.35 shows us that the the correction to the \( s \)-wave gap depends on the value of the the coupling constants \( \gamma_{B\alpha} \) and a case can be found where the anti-aligned \( s \pm \) gap is characterized by a considerably smaller \( \gamma_{B\alpha} \) when compared to the aligned gap. This condition can result a net negative proximity effect on the \( s \)-wave superconductor, effectively suppressing it. Figure 3.7 shows the dependence of \( \tilde{\Delta}_{s,0} \) on the coupling constants \( \gamma_{B\alpha} \).

![Figure 3.7: Correction to the s-wave gap \( \tilde{\Delta}_{s,0} \) as a function of the coupling constants \( \gamma_{B\alpha} \). We can see regions around where \( \gamma_{B1} \) and \( \gamma_{B2} \) are comparable where instead of a positive, there is a negative proximity effect on the s-wave superconductor. The 2 figures explore the cases when the s\pm gaps are equal and when they are different.](image)

Finally, an approximate analytic expression is obtained for the change in the DOS for the s-wave super-
conductor $\delta N_s(E, x)$ using calculated evaluations of the correction to the Green’s function $\tilde{\Phi}_s(E, x)$:

$$\delta N_s(E, x) \approx \pi T_c^+ \frac{\zeta^2}{d_s} \frac{E \Delta s_0}{(E^2 - \Delta^2 s_0)^{3/2}} \sum_{a} \frac{\Delta s_0 - \Delta a_0}{\tilde{\gamma}_{Ba} \sqrt{|\Delta s_0| - E}} \Theta (|\Delta s_0| - E)$$

(3.36)

Again, we can see that an aligned state (positive $\Delta_a$) will induce enhancements in the DOS of the $s$-wave superconductor while anti-aligned states (negative $\Delta_a$) will induce suppressions. To see more realistic results past the assumptions of the weak-coupling regime, numerical solutions must be found. For the case of an $s$-wave superconductor forming an aligned state with an $s$± superconductor with non-equal gaps and coupling constants, figure 3.8 shows the effects of different values of $\gamma_{Ba}$ in the DOS the $s$-wave superconductor.

![Figure 3.8](image)

Figure 3.8: Examples of DOS spectra in aligned states with varying coupling constants $\tilde{\gamma}_{Ba}$. Subfigure (a) shows the spectrum for $N_s$ for the case where the smaller s± gap, $\Delta_2$, is anti-aligned with respect to $\Delta_s$ but its interface coupling constant $\tilde{\gamma}_{B2}$ is larger than $\tilde{\gamma}_{B1}$ creating a negative proximity effect. Subfigure (b) shows a positive proximity effect taking the inverse situation as in subfigure (a). Subfigures (c) and (d) show the corresponding DOS spectra for the s± gaps both close to the interface and away from it. Subfigures (e) and (f) show the evolution of the corrections to $N_s$ as a function of the varying parameter $\tilde{\gamma}_{Ba}$. Notice the now characteristic step shapes between $\Delta_1$ and $\Delta_2$. Figure taken from [57].
Figure 3.8 shows some interesting features that were not present in the original analysis from section 3.2.1. First of all, we can see that in the aligned state, although peaks and dips in $N_s$ are still present showing positive and negative proximity effects, they are now forming step-like structures with amplitudes depending on the specific interface coupling constants. Secondly, a negative proximity effect can now be detected in the value of $\Delta_s$ depending on which of the $s\pm$ gaps becomes preferably aligned with the $s$-wave gap. This effect could be of help in the evaluation of the $s\pm$ model as a valid pairing theory for FeSC’s since a positive proximity effect is rather ubiquitous when a small-gap superconductor is placed in proximity with a large-gap one, however a suppression of the small-gap superconductor can only happen when the multiband superconductor has large gaps with alternating signs.
Chapter 4

Materials and Methods

In this chapter we cover the particulars regarding our sample preparation protocols, our experimental setup and the tools used for the measurement analysis. We start by describing the process through which Ba122 crystals are processed into samples for the two distinct experiments. We follow by describing the cryogenic setup used to bring the samples to the operating temperatures and the modifications to the base refrigerator needed to achieve the necessary measurement sensitivity and accuracy. Finally, we describe the electronics used in the setup and the tools used for the data analysis.

4.1 Sample Considerations and Fabrication

4.1.1 Crystal Growth

Co-doped Ba(FeAs)$_2$ crystals were obtained from Paul Canfield’s group in Iowa State University in the underdoped, optimally-doped and overdoped regimes. These crystals were synthesized through the self flux method [58, 59]. Through this method, stoichiometric amounts of the different components of the crystal structure are mixed with a common solvent to all of them, also called a flux. In particular to Ba122 crystals, FeAs acts as the common solvent or flux, to which pieces of metallic Ba and CoAs powder were added in ratios according to the expected doping levels. The mixture is sealed in a quartz ampule with a $\sim 1/3$ atm of Ar gas, brought to a temperature of 1180 °C and slowly cooled down to 1000 °C over the course of 36 hours. The particular temperature is selected such that, while still higher than the melting point of the flux, it allows for the nucleation of Ba122 crystals with the required composition. After allowing time for the growth of crystals, the ampule is broken and the flux is drained through a quartz wool, filtering out the crystallized compounds.

All the crystals underwent a characterization stage through powder X-ray diffraction, wavelength dispersive X-ray spectroscopy and transport measurements to record the lattice parameters, the elemental analysis and the resistivity/transport characteristics, respectively, as a function of doping.

A picture of a typical crystal can be seen in figure 4.1. Most crystals had dimensions in the order of
$\sim 5 \times \sim 5 \times \sim 0.5 \text{ mm}^3$ showing irregular profiles. X-ray diffraction was used on these crystals to find the orientation of the main axes before they were processed.

Figure 4.1: Example of a typical Ba122 crystal in as-grown form.

4.1.2 Sample Preparation

In order to fabricate either Josephson junctions or tunnel junctions on the surface of Ba122 crystals, a very flat and clean surface must first be obtained. This requirement results in 2 specific conditions to be met:

1. A clean and unperturbed surface on which other materials could be evaporated or sputtered. An as-grown surface would be ideal for fabrication because of the pristine nature of its crystal structure.
2. The selected surface must be perpendicular to the direction in which electronic tunneling will be required.

Unfortunately, there is evidence that the presence of monovalent and divalent metals in the composition of the Fe-based superconductors of our interest favors the creation of surface oxides that degrade the quality of the crystal faces in a way we cannot control [60]. Thus, we were required to obtain a fresh surface just before patterning any structures on the crystal surface. As seen in chapter 1, the Fe-As planes that make up the structure of the Fe-based superconductor form quasi-2-dimensional crystalline planes that are weakly
bound along the c-axis. This structural characteristic is favorable when planes perpendicular to the c-axis are required, since mechanical cleaving brings out very flat intact surfaces, but otherwise, we need to use manual polishing to achieve the necessary planes.

For the case of Co-doped Ba122 crystals, in order to obtain flat surfaces perpendicular to the a-b planes, lapping paper with a grain size ranging from 5 \( \mu m \) to 0.3 \( \mu m \) was used to systematically erode a flat or round face on a crystal to a mirror-like finish. For this process, pieces were first cut to a rough size with a razor blade, then fixed to a rotating aluminum piece using Crystalbond\textsuperscript{®} and polished with a piece of lapping paper.

In reference to the substrate used for all samples, 1 cm\(^2\) chips were cut out of a 300 \( \mu m \)-thick polished Si wafer. Chips were cleaned before mounting any crystals through consecutive baths of PG Remover (75 °C, overnight, ultrasonic cleaner), Acetone (60°C, 20 minutes, ultrasonic cleaner) and IPA (room temperature, 5 minutes, ultrasonic cleaner). Before the cleansing baths, the chips were also scratched with a diamond scribe in an area where the sample crystal will be placed in order to increase the surface area for better adhesion with the gluing agent. After the IPA bath, the Si chips were blown dry with \( \text{N}_2 \).

Polished crystals were mounted on a polished Si chip using a small amount of Pyralin\textsuperscript{®} polyimide. The mounted crystals were placed on a hot plate to cure the adhesive following a 140°C/min ramp from 60°C to 200°C over 75 minutes. After curing is complete, the sample chips would be cleaned again in IPA (room temperature, 5 minutes, ultrasonic cleaner) and blown dry just before masking.

The masking of macroscopic features on the sample chips was done through the use of Riston\textsuperscript{®}, a dry resist that can be cut in strips to selectively mask areas where it non-specifically attaches to the surface of interest. Riston\textsuperscript{®} has a low vapor pressure(< 10\(^{-7}\) mTorr), making it ideal for masking where the deposition of later films will be done in either a sputtering or a thermal evaporation system. After the thin-film deposition has been completed, a lift-off procedure can be done by simply peeling off the adhered strips.

**Josephson Interferometry**

For the purpose of probing the pairing symmetry of Co-doped Ba(FeAs)\(_2\) crystals through Josephson interferometry, Superconductor-Normal metal-Superconductor (SNS) Josephson junctions were fabricated on surfaces perpendicular to the c-axis in 2 configurations, as seen on chapter 1:

1. **Edge junction.** This configuration refers to Josephson junctions fabricated on a single flat facet on the crystal set to probe a very small set of \( \mathbf{k} \) around the Ba122 crystal’s Brillouin zone.

2. **Corner junctions.** This configuration refers particularly to a geometry proposed in order to probe
the Brillouin zone of the Ba122 crystal with a set of $\mathbf{k}$ that span a 45° angle [47]. For this configuration, 2 facets in the crystal were polished with this relative angle between them and a Josephson junction was fabricated in the corner area.

After multiple attempts trying to create a clean corner geometry, we came to the conclusion that the polishing a corner on Ba122 crystals resulted in a very unreliable surface. Thus, a variation of this scheme was tried where, instead of edge and corner surfaces, we would polish a single cylinder-like surface with its radial component being perpendicular to the c-axis of the Ba122 crystal. This variation allowed for polishing in a single step, reducing the overall damage of the resulting crystal planes.

A consequence of this sample fabrication process is that Josephson junctions on a cylindrical surface probe a solid angle in k-space, rather than the ideal single k-vector. Thus we redefine the types of Josephson junctions we fabricate as:

1. **Edge-like junctions.** In this configuration, the solid angle in k-space that the Josephson junction covers probes a region of the order parameter in the Ba122 crystal that does not change significantly in magnitude and/or phase. Thus, measurements on these structures should yield results similar to those of edge junctions.

2. **Corner-like junctions.** In this configuration, the solid angle in k-space that the Josephson junction covers probes a region of the order parameter in the Ba122 crystal that changes abruptly or significantly in magnitude and/or phase. Thus, measurements on these structures should yield results similar to those of corner junctions.

Taking a single Ba122 crystal mounted on a Si chip as seen in section 4.1.2, we attempted to fabricate a series of both edge-like and corner-like Josephson junctions by masking areas on the polished facet of the sample crystal. The general dimensions of these structures were in the order of 300 $\mu$m–500 $\mu$m in width by $\sim$ 500 $\mu$m in height.

The Josephson junctions were fabricated in a single session in a thermal evaporator. The masked chips would first undergo 30 seconds of Ion Milling\(^1\) to remove any reminder organic contaminants on the crystal surface, followed by the thermal deposition of 150 nm of Cu, to work as a normal metal barrier, and 0.8–1 $\mu$m of Pb/In (20:1 by weight) as the conventional superconductor to complete the junction. Precautions were taken in order to ensure complete coverage of the unmasked areas on the crystal by rotating the sample stage during the evaporation. Following the material deposition, the masking was removed and indium pads or Al wire-bonds were used to fix connections to the pads on the chip. Figure 4.2 shows typical samples prepared under this protocol.

\(^1\)250 V Cathode voltage, 50 mA Beam current, 50 V Accelerator voltage, $\sim$ 50 cm distance from gun to target.
Proximity-induced DOS signature

For this experiment, we need to probe the DOS spectrum of a conventional s-wave superconductor in proximity with a Ba122 crystal. In order to do this we chose to build Superconductor-Insulator-Superconductor (SIS) tunnel junctions in which one of the superconductive electrodes would be in proximity with the Ba122 crystal. The choice of materials and dimensions came from the theoretical background described in chapter 3 and described by Koshelev and Stanev [51] and can be summarized as follows:

1. The DOS measurement must be done in a temperature regime where $T_{\text{meas}} \ll T_{C,s}^\pm$, so our s-wave superconductor must have a $T_{C,s} > T_{\text{meas}}$.

2. The DOS measurement will be done while the s-wave superconductor is in a quasiparticle regime, thus, the value of the superconductive gap $\Delta_s$ of this material should be significantly below the region of interest $5 \text{ mV} < V_{\text{interest}} < 25 \text{ mV}$ that comes from previous ARPES measurements [61, 26].

3. The thickness $d$ of the s-wave will be such that $d_s \ll \xi_s$ where $\xi_s$ refers to the s-wave superconductor’s coherence length.

Since in Ba122 crystals $T_{C,s}^\pm \sim 20 \text{ K}$, all of our measurements should be carried out in Liquid Helium (LHe) environments, which are readily available. However, while condition 1 still leaves a large window of options in terms of choices for an s-wave superconductor, condition 2 restricts the list of usable superconductors; the reason is that out of our higher $T_{C,s}$ superconductors (i.e. Pb, Nb, MoGe) most of them have values for $\Delta_s \sim V_{\text{interest}}$. Moreover, several of these s-wave superconductors are also strong electron-phonon scatterers, which in our DOS measurements, would be responsible features around $\Delta_s$ that could compete
in amplitude and position in the \( V_{\text{bias}} \) axis with the signals we are attempting to measure.

After analyzing the former arguments, we turned our attention to Al as our most viable option for an s-wave superconductor. Despite its low \( T_{\text{C,Al}} \simeq 1.2 \, K \), which would require at least a \(^3\)He refrigeration, this material offers several advantages over other options. First of all, \( \Delta_{\text{Al}} \simeq 190 \, \mu\text{V} \ll \Delta_{s\pm} \), which in combination with the fact that Al is a weak electron-phonon scatterer, plays in our favor meeting conditions I. and II., given the appropriate cooling is provided. Second of all, \( \xi_{\text{Al}} \approx 1\mu\text{m} \) for bulk material and \( \xi_{\text{Al}} \approx 100\text{nm} \) for actual thin films, giving us plenty of room to play with \( d_{\text{Al}} \) since condition III. only depends on \( \xi_s \). Lastly, protocols to fabricate SIS junctions in the form Al/AlOx/Al are readily available in our group [62].

The fabrication of the SIS tunnel junctions was done in 3 steps of sputtering. Starting with a mounted Ba122 crystal on a Si chip, we masked the crystal with Riston\(^\circ\) to define the area of the SIS junction and the bottom electrode. We proceed to do a brief Ion Milling exposure followed by sputtering of 50–70 nm of Al to define the bottom electrode. See figure 4.3a. The first Riston\(^\circ\) mask is at this point removed and, using a micro-manipulator, we placed 5 \( \mu\text{m} \) diameter polystyrene microspheres\(^2\) to act as a local mask. See figure 4.4. We now cover the entire chip with \( \sim 150 \, \text{nm} \) of SiO\(_2\) to insulate the bottom electrode except on the areas that are now covered with the microspheres.

The same micro-manipulator was then used to remove the microspheres and reveal the via-hole in the SiO\(_2\) insulator and a second step of Riston\(^\circ\) masking is done to define the geometry of the top electrode in the SIS junctions. Finally, inside the sputtering chamber, Ion Milling is done to clear the surface AlOx layer covering the bottom electrode, O\(_2\) is introduced to grow now a controlled oxide and 200 nm of Al are sputtered to complete the top electrode. Figure 4.3b shows a finished sample created for the proximity-coupling experiment. False color is used to identify the overlapping electrodes and the position of the devices.

After taking several data sets using this fabrication procedure, a concern was raised regarding the degradation of the surface on the FeSC during the curing phase of the adhesive. Since the cleavage procedure to obtain fresh surfaces on the Ba122 crystal is done on air, an oxide layer is expected to form, however, our experience managing these crystals indicates that we have a window of a few hours at room temperature before the degradation of the recently obtained surface is degraded significantly. Nevertheless the exposure to higher temperatures and the solvents in the polyimide solution during its curing phase accelerates this degradation until it is noticeable to the naked eye.

\(^2\)02705-AB Polystyrene DVB microspheres, 5 \( \mu\text{m} \) dia suspended in DI water. Purchased from Structure Probe, Inc.
Figure 4.3: Proximity coupling sample. 4.3a shows bottom electrodes and insulator layer. For this particular sample, we can see 2 Al electrodes coming in contact with the crystal and 2 Al electrodes ending in the Si substrates to serve as reference tunnel junctions. This crystal was coated with Pd and Ag before mounting to reduce degradation due to the heat in the curing process. 4.3b shows the finished sample after the via holes are done and the top Al electrode is deposited. False color added to show overlapping electrodes and the approximate region where the via holes were placed.

Figure 4.4: Use of polystyrene microspheres as lithography masks. The shadow effect of the sphere during the sputtering of SiO$_2$ creates a via hole in the insulator. In the AFM scan of the via hole, the area in blue represents the exposed bottom surface with an area $A \sim 3\mu m^2$. 
Thus for the last set of samples we present, we adopted a capping procedure to ameliorate the final quality of the exposed crystal surface. This capping was done in two ways after the selected crystal was cleaved:

1. A thin film (∼ 20nm) of Al was sputtered directly on the exposed surface. This capping procedure ensured a direct contact and high coupling between the conventional superconductor and the multiband superconductor.

2. A thick film (∼ 400nm) of Ag was sputtered directly on the exposed surface. This step was done to attempt a low coupling regime between the conventional superconductor and the multiband superconductor through the presence of a normal metal barrier between the two.

After this step, crystals were cleaned in PG-remover, Acetone and Isopropyl alcohol to remove organic residues and, then, mounted on the Si chip using polyimide in the same fashion as described above. Further fabrication steps were not altered by the inclusion of this capping procedure.

Wiring and final liftoff are done simultaneously with the help of a wedge bonder, leaving the sample ready for a cooldown.

4.2 Cryogenics

Initial Josephson interferometry experiments were carried out using a $^4$He refrigerator consisting of a vacuum and liquid-$N_2$ insulated dewar and an cold finger with an inner vacuum can (IVC) where the sample would reside. Using this simple construction we were able to mount a Quantum Design® SQUID with leads sent inside the vacuum can through a sealed through-hole. Variable pumping on the $^4$He bath, in combination with a local heating resistor provides us with temperature control between ∼ 1.2K → 20K. This system was designed with the objective of a fast turn around rate; a typical load of $^4$He may last ∼ 8 hours when no pumping was done on the bath.

Samples were glued to PCB sample stages and bonded using a Al wire wedge bonder. However, NbTi wires to be connected to the SQUID would be secured in place using In pads placed manually. Current and voltage lines go through cold resistors at the temperature of the bath to minimize thermal noise and passive RC filtering was added at the break-out box for increased noise reduction. Magnetic shielding was done using a Pb sleeve around the IVC and sheets of $\mu$-metal around the $^4$He dewar. Measurements were carried inside a Faraday-cage screen room with signal lines going inside through connectors anchored to one of the room’s walls.
For the proximity effect experiment, all measurements were completed in a $^3$He refrigerator in order to stay significantly below $T_C$ of the Al contacts ($\sim 1.2\ K$). In this kind of He-based refrigerator, a volume of $^3$He, an isotope of He with only 1 neutron, is condensed into a liquid and, through evaporative cooling, taken down to a temperature around 250–300 mK. A sample is put in contact with the liquid He3 reservoir and cooled as well through direct thermal conduction.

Our particular refrigerator is an Oxford® Heliox $2^VL$ Sorption pumped $^3$He Insert. Figure 4.5 shows the principle of operation behind our $^3$He refrigerator. The system consists of a closed circuit that contains the gaseous $^3$He and a cartridge of activated charcoal acting as a sorption pump (SORB). This closed circuit ends in a small can where the $^3$He can be collected, once it is condensed, called the $^3$He pot. Just above the $^3$He pot and surrounding the line that leads into it, there is a small container, called the 1K pot, used in the condensation of $^3$He. When the system is cooled down and placed inside a liquid $^4$He dewar, a heater keeps the SORB at a temperature of around 40 K while the 1K pot is partially flooded with liquid $^4$He and the gaseous space is pumped down with an external pump. The evaporative cooling takes the $^4$He inside the 1K pot to a temperature of around 1.5 K, giving the $^3$He in direct contact to the 1K pot a cold surface on which to condense, so that by gravity, it starts collecting in the $^3$He pot.

In order to take the system to base temperature, once the liquid $^3$He is in the $^3$He pot, the heating on the SORB stops and, through external lines, $^4$He starts flowing around it from the reservoir, cooling down the SORB to about 5 K. At this point, the SORB starts pumping on the gaseous phase of the $^3$He reserves and the liquid $^3$He temperature goes down through evaporative cooling. The final temperature on the $^3$He pot can be regulated by either directly heating the $^3$He stage with an external heater, or by controlling the temperature of the SORB through a heater, effectively changing its pumping power. The $^3$He pot will maintain its cooling power until all liquid $^3$He has evaporated, at which point, the condensation procedure must be started over to recover the $^3$He in liquid form. For this reason, this type of $^3$He refrigerator is called a single shot refrigerator.

Our particular refrigerator can operate with a 15 liter transfer of $^4$He for around 18 hours and a single base-temperature shot for about 5-6 hours. The actual base temperature and the duration of the operation at this point depends on the heat load from the sample in the form of thermal mass, dissipated power and contact with the external 4.2 K $^4$He bath.

Our samples are thermally connected to the $^3$He pot through a copper sample stage. Each fabricated Si chip is glued down to a PCB that gets thermally anchored to the sample stage. Wiring coming from the outside gets first thermally anchored with cold resistors kept at the bath temperature, then around the 1K pot and, finally, around the $^3$He pot before reaching the sample. Final stages of wiring are done with
Figure 4.5: Principle of operation of a $^3$He refrigerator. The diagram on the left shows the condensation of the $^3$He into the $^4$He pot by keeping the SORB at 40 K and cooling the $^3$He through the 1K pot. The diagram on the right shows the evaporative cooldown of the liquid $^3$He by the pumping action of the SORB while kept under 10 K.

manganin wire to reduce the heat load on around the $^3$He stage.

In order to reduce noise levels during measurements, different types of insulation have been provided. In terms of magnetic shielding, the sample space is first enveloped by a Pb can that will be superconducting at liquid He temperatures, providing static magnetic field protection through the Meissner effect. Around the liquid He reservoir, a double layer of Mu-metal has been placed to re-route magnetic fields while the Pb can is still warm. In terms of thermal shielding, a brass can is placed around the sample and thermally anchored to the sample stage in order to prevent the introduction of noise through radiation from the liquid He bath. When a magnetic field is needed, instead of the can, a coil is placed around the sample, which will also be anchored to the sample stage, shielding the sample from the thermal noise coming from the liquid He bath.

### 4.3 Electronics and Data Analysis

The measurement setups used in the measurement of the pairing symmetry of Ba122 crystals are based on a 4-terminal measurement of IV curves or $dV/dI$ vs V curves.

In the case of the Josephson interferometry experiment, as seen on figure 4.6a, a current supply was used to drive SNS Josephson junctions from their superconducting state into their dissipative state. A preamplifier
Figure 4.6: Circuit diagrams for pairing symmetry experiments. Figure 4.6a refers to the setup used to obtain IV curves and diffraction patterns in Pb/Cu/Ba122 Josephson junctions; figure 4.6b shows a similar setup but using a SQUID as a more sensitive voltage meter.

Figure 4.7: Circuit diagram for Proximity-Induced DOS signature. This figure shows the setup used in the measurement of the DOS spectrum of Al/AIox/Al tunnel junctions in proximity with Ba122 crystals.

was used to monitor the state of the SNS junction across that transition as the current was swept in order to record the value of the critical current \( I_c \). The value of the applied current was obtained from a second preamplifier measuring the voltage drop across a resistor in series with the current supply.

However, due to the low normal state resistance \( R_N \) of SNS junctions because of the inherent transparency of Cu as a barrier, a SQUID is used in order to boost our sensitivity when measuring the voltage across the terminals of our SNS junction. The SQUID is adapted as a voltmeter through the following procedure: a standard resistor \( R_s \), usually made of thin brass foil, and an inductor, a loop made of NbTi wire, are connected in parallel to the SNS junction under scrutiny. A SQUID is then inductively coupled to this RL circuit through another pick-up loop. A diagram of this coupling can be seen in figure 4.6b.

When the SNS junction is in its supercurrent state, all current between the common terminals flows through the junction and none through the SQUID-coupled branch, giving us no signal through the inductively-coupled SQUID. When the SNS junction transitions into its voltage state, a current-divider circuit is now in action, so a fraction of the total circulating current goes through the SQUID coupled branch. Since a
SQUID is an extremely sensitive current sensor, and by knowing the precise value of $R_N$, we can compute the value of the voltage across terminals. With appropriate magnetic shielding, this measurement can be done with very low noise floors.

A Helmholtz coil was added to the circuit to be able to record the modulation of $I_c$ as a function of applied magnetic flux $\Phi$, what we call $I_c\Phi$ curves, or as a first approximation, what we call $V\Phi$ curves. This modulation corresponds to the Fraunhofer pattern measured in SIS and SNS Josephson junctions with conventional superconductive contacts. As a first approximation to the modulation of $I_c$, we start with a $V\Phi$ curve. This plot is taken by current biasing the Josephson junction under analysis at a point $I_{bias}$ just above $I_c$ into the junction’s voltage state. By varying the applied magnetic field, with its corresponding modulation in $I_c$, we see a change in the measured voltage that runs -roughly- inversely with the value of the critical current (see figure 4.8a for a schematic representation). This curves are easy to take, however their sensitivity is highest when $I_c$ runs close to its maximum value and the voltage measurement is done at a point of high differential resistance, but it decreases when $I_c$ gets close to zero. Thus they are used to see details on the main lobes in a diffraction pattern but they are not adequate to see details close to the minima in $I_c$.

On the other hand, to record $I_c\Phi$ curves for a given Josephson junction, first we apply a biasing current until the junction transitions into a dissipative state, keeping the device driven just above $I_c$ and at a small voltage $V_{bias}$. Then, a PID loop is started on the current supply driving the junction to keep $V_{bias}$ constant as we slowly sweep $\Phi$ ($\sim 100 \text{ mOe} \times A_J/\text{min}$) with another current supply. By keeping track of the output of the PID control signal as $\Phi$ is scanned, we construct our $I_c\Phi$ patterns (see figure 4.8b for a schematic representation). This curves capture the full detail of the modulation of $I_c$ however they require more active elements to work correctly. In particular, this curves are susceptible to a poorly tuned PID control loop that is unable respond to the speed of particular modulations of $I_c$ requiring slower field sweeps and active user control.

To facilitate the suppression of current noise in any of the measurements, all current supplies are battery operated, effectively eliminating 60 Hz noise. In addition to this, noise filtering was done passively through the use of low-pass RC filters tuned at 1 kHz on the current input lines and through the integrated low-pass filters tuned at 300 Hz on the preamplifier stages. During the data acquisition, averaging was also used to reduce noise in the recorded signal.

Measurements in this experiment were carried out using LabView routines to control the data acquisition, the output control signals and the signal averaging/data output.

$^3 A_J$ is defined as the effective area through which magnetic flux $\Phi$ threads the Josephson junction, as seen in section 3.1.
Figure 4.8: Diagram showing how a VΦ and an I_cΦ curves are obtained for Josephson junctions. A VΦ curve is taken under a constant current bias slightly above the maximum I_c by monitoring the voltage reading across the junction while the applied magnetic field modulates the critical current. An I_cΦ curve is taken at a constant bias voltage just above the transition into the voltage state by monitoring the necessary bias current while the applied magnetic field modulates the critical current.

For the case of the measurement of the DOS spectrum of Al/AlOx/Al tunnel junctions in proximity with Ba122 crystals, the current supply was implemented through the sum of a DC voltage signal from a power supply with a small AC modulation from a Lock-In Amplifier which would then be passed through a large bias resistor R_{bias}. A diagram of this circuit can be seen in figure 4.7. The resulting voltage signal across the terminals of the tunnel junction is then analyzed with a preamplifier with a 100 Hz low-pass filter, to obtain the DC bias voltage, and with a Lock-In amplifier tuned at 17 Hz to obtain the differential resistance dV/dI signal. After the acquisition, the dV/dI data is inverted to obtain dI/dV ∝ DOS.

For this measurement, noise reduction was implemented through the use of low-pass filters in the input lines and taking advantage of the sensitivity of the Lock-In amplifier combined with extensive averaging of the measured points. In our first approach, our measurements were being done at a Lock-In frequency of 91.1 Hz, however, we noticed that our signal-to-noise ratio increased significantly after we reduced our measurement frequency to 17 Hz. The reason for this change could be the combination of the large normal-state resistance of our devices with the inclusion of parasitic capacitance creating an effective low-pass filter on the device. In this transition to lower measurement frequencies we had to compromise completion time for improved data quality; this change, though, affected our measurement time from a few minutes for a full scan to a 2-3 hours. We found our signal-to-noise ratio increased as well after the addition of the radiation shield mentioned in section 4.2, by improving the sample temperature stability.

All data acquisition and management, as well as output control, was done through programming in Matlab, using DAQ communication libraries written by Christopher D. Nugroho. Plotting and further analysis of data sets was done using Origin. In particular, some data sets showed the presence of modulations...
in our signals at very particular frequencies. Noise filtering for those cases was done numerically by taking
and FFT of the data and filtering out the specific affecting frequencies through a low-pass or a notch filter
routine; this filtering was done in Origin as well.
Chapter 5

Results and Discussion

In this chapter we present the results and analysis of the data obtained from our Josephson interferometry and Proximity-induced signatures of $s\pm$ superconductivity. Here we present the data we obtained from experiments and make the connection to the models seen in chapter 3 in the hopes of discerning which of the current pairing models adjusts better to the data.

In first instance, we will look at the Josephson interferometry experiments applied to the Co-doped Ba122 crystals in an effort to elucidate the presence of a strong gap anisotropy and, possibly, a sign change in the superconducting order parameter. Then, we move to describe the results of the measurement of the DOS of a thin film of an $s$-wave superconductor in proximity with a Co-doped Ba122 crystal; we analyze the dependence of these results on the surface and bulk properties of the FeSC and try to separate the results according to coupling regimes.

5.1 Josephson Interferometry on Ba(Fe$_{1-x}$Co$_x$As)$_2$ crystals

With the Co-doped Ba122 crystals obtained from Paul Canfield at Iowa State University, we proceeded to make samples consisting of SNS Josephson junctions on corner and edge geometries (see section 4.1.2 for details) to be characterized through Josephson interferometry. This measurement implies looking for supercurrents in the fabricated junctions and analyzing the dependence of the critical current $I_c$ on applied magnetic flux through the action of Helmholtz coil. IV (Current vs Voltage) curves are first taken to search for a supercurrent and, following that, $I_c$ modulation plots, or diffraction patterns, are recorded. Diffraction patterns are presented in the shape of either a $V\Phi$ curve or an $I_c\Phi$ curve, depending on the availability of equipment (see section 4.3 for further details) with the $x$-axis referring to the applied flux and the $y$-axis either to measured critical current or to measured voltage under constant current bias.
5.1.1 Results and Analysis

Starting with optimally-Co-doped Ba122 crystals, we polished the samples to show facets that would align with either the \( a \) or \( b \) axes of the crystal or with plane forming a 45\(^\circ\) angle with the former facets. Corner and edge junctions were fabricated on them. When no obvious facets were found, polishing was used in order to create them or to create a continuous curved surface on which several Josephson junctions could be fabricated, with each individual junction probing a small solid angle in the BZ.

IV curves and diffraction patterns were obtained on these samples. For a typical measured Josephson junction, the IV curve is shown with superimposed trace and retrace measurements. All results shown were carried out using a regular \( ^4 \)He refrigerator with an operating temperature of \( 1.5K \leq T \leq 4.2K \).

A typical SNS Josephson junction shows the behavior represented in figure 5.1. We can see the SNS behavior resembling a resistively shunted SIS junction. Due to the variable (and usually low) normal-state resistances of these devices, a SQUID was used to monitor some of their transition into the voltage state, when a preamplifier was not sensitive enough. Devices fabricated with the previously described methods show a wide value of critical currents, as seen in figure 5.2, despite using the same processing protocols for several samples, the properties of Josephson junctions fabricated on Ba122 crystals vary within several orders of magnitude, resulting in measured \( I_c \) as low as a few hundred nanoamperes to several milliamperes.

![Figure 5.1: IV curve of one of the measured SNS Josephson junction. A SQUID was used to monitor the voltage between terminals of the junction.](image-url)
After finding Josephson junctions with a suitable $I_c$ we proceeded to apply a magnetic field in an axis perpendicular to that of the devices to look for $I_c$ modulation. As seen in section 3.1, Josephson interferometry is particularly sensitive to changes of sign in the overall order parameter, as in $d$-wave superconductivity, exhibiting a characteristic double central peak in the diffraction data. Other types of order parameter symmetry models, like $s$-wave and extended $s$-wave will show a central peak in the diffraction data, but changes in the side lobe structure. Thus, by constructing edge- and corner-like junction geometries, we can characterize the order parameter in Ba122 crystals as belonging to $d$-wave or some type of $s$-wave depending on the measured central lobe structure.

For edge-like geometries we find a set of patterns with a single central lobe and Fraunhofer-like structure. Figures 5.3 and 5.4 (red line) show examples of edge-like Josephson junctions: a central featureless lobe that ends in a minimum in $I_c$, side lobes with amplitudes much lower than the central lobes and periodic minima in $I_c$. In particular, we can see that even though both samples were fabricated using similar size scales, the periodicity in the field axis is different by around a factor of 5, indicating us that, considering the same SNS composition (and effective gap), the area of the junction in figure 5.3 is about 5 times smaller than for the junction represented by figure 5.4, which is consistent with the difference in the magnitudes of $I_c$.

Josephson junctions that were fabricated on corners, or designed to be corner-like, show a distinctively different behavior both, respect to the edge junctions and among themselves. The reason for this is that any asymmetry in the Josephson junction will change the contributions from the 2 distinct gap regimes to the final diffraction pattern. Nevertheless, we are looking at the presence of single/double peak(s) around
Figure 5.3: $I_c\Phi$ plot showing a diffraction pattern of an edge-like Josephson junction. Inset shows corresponding IV curve.

Figure 5.4: $I_c\Phi$ plot showing a diffraction pattern of an edge-like Josephson junction after FFT filtering. Inset shows corresponding IV curve.
the zero-flux point, change in the relative amplitude of side lobes and the presence of raised minima in $I_c$ when compared to a Fraunhofer pattern. Figures 5.5, 5.6 and 5.7 are examples of the diffraction patterns obtained with these types of structures. The first thing we notice is that no double-peak profiles appear around the zero-flux point in the plot, indicating that the gap around this angular profile doesn’t change signs. The second thing we see is additional side lobe structure which, recalling from section 3.1, indicates a anisotropic gap spanning the 2 crystal facets under analysis. Those 2 characteristics point towards extended $s$-wave models like $s\pm$ and $s++$, but this information is not enough to distinguish between the two.

![Figure 5.5: $I_c \Phi$ plot showing a diffraction pattern of an corner-like Josephson junction. Notice the elevated side lobes and the high amplitude of of the modulations after the first $I_c$ minimum. Inset shows corresponding IV curve.](image)

The comparison that is necessary to distinguish between the extended $s$-models through Josephson interferometry requires at least 3 junctions on the 2 facets used for a corner junction (2 edge-like junctions and a corner-like junctions) with the same fabrication parameters. Then, a comparison like the one in figure 3.5 can be made and one pairing symmetry model can be chosen over the other. However, as we will see, this requirement could not be met because of fabrication problems that limited our experimental output. Nevertheless, out of the number of Josephson junctions we were able to fabricate, an $I_c R_N$ plot was constructed separating corner from edge junctions. Figure 5.8 shows the behavior of the 2 types of junctions as a function of $I_c$. Despite the broad spread of $I_c R_N$ values, some clustering is evident with

1Not all the fabricated Josephson junctions with measurable critical currents could be added to this plot since some of them showed pronounced curvatures in their linear resistance regimes due to sample heating. This curvature prevented us from
Figure 5.6: $V\Phi$ plot showing a diffraction pattern of an corner-like Josephson junction. Notice the large amplitude of the side lobes and the complex structure of the central lobe. Inset shows corresponding IV curve.

Figure 5.7: $I_c\Phi$ plot showing a diffraction pattern of an edge-like Josephson junction after FFT filtering. The low-$f$ envelope shows that the first minima are local and the second minima are lower in magnitude, indicating raised nodes. Inset shows corresponding IV curve.

extracting a representative value for $R_N$ necessary for this analysis.
corner junctions exhibiting lower typical $I_cR_N$ values than the edge equivalents. This clustering supports at first glance a notion that the effective gap probed by corner junctions is lower than the one edge junctions probe, supporting an $s\pm$ arrangement of gaps, however, there is not enough collected data in this analysis to make a definitive statement.

Figure 5.8: $I_cR_N$ product of Pb/Cu/Ba122 SNS edge or corner Josephson junctions as a function of $I_c$. We can see clustering in the data with $I_cR_N$ products behaving differently for corner vs edge junctions.

5.1.2 Experimental limitations

In our effort to fabricate and characterize Josephson junctions with reproducible and tunable properties using Ba122 crystals, we were faced with problems regarding the surface quality of our crystals that prevented us from obtaining consistent fabrication protocols that would allow for across-sample comparisons. From the literature (see [60]), we understand the surface degradation and oxidation in FeSC’s, which act in detriment to the fabrication of Josephson junctions, occurs in an inhomogeneous and uncontrolled fashion, which when coupled with the mechanical damage done to the crystal to obtain the necessary facets for our experiment, result in surfaces with undetermined crystal structure and electrical properties.

The three main effects that surface degradation favored in our structures were: high surface resistance (dead layers), intermittent surface contact and pinholes. The first of these effects resulted in mainly the fabrication of Josephson junctions where a critical current was either non-existent or too small to be accurately
measured, considering our electrical noise floor. In our IV curves, these devices show only ohmic behavior with resistance values that could not be correlated to sample doping or fabrication protocols.

The second effect we faced was the splitting of the FeSC surface into interfaces with different degrees of transparency on which Josephson junctions were fabricated. This splitting caused single Josephson junction geometries to turn into SQUID-like structures where the $s$-wave superconductor used to contact the FeSC through multiple areas within a single contact. The multiple SQUID areas in conjunction with the applied flux created diffraction patterns with the characteristic SQUID interference patterns superimposed on single junction interference patterns. Figures 5.4 and 5.7 show a case where Josephson junctions split into two junctions, one of them much larger than the other, and thus, dominant over the small one. In this case, the SQUID periodicity can be seen in the high-frequency oscillations modulating a much lower frequency single-junction pattern.

Cases like this can still be of use for our analysis because since the amplitude of the SQUID oscillations is much smaller than that of the single junction interference pattern and its characteristic frequency significantly higher and constant, we can filter them out using a simple low-pass or a band-block numerical routine. In particular, for the data in figures 5.4 and 5.7, we reviewed the data in the frequency domain using a Fast Fourier Transform (FFT). The SQUID oscillations showed a distinct peak in the transformed data, letting us set up a numerical filtering routine with a roll-off frequency just below that of the SQUID oscillations. The filtering in general was either done through a low-pass filter or a notch (band-stop) filter after isolating the peaks in the PSD corresponding to SQUID oscillations in the $I_c\Phi$ data. Figure 5.9 shows the FFT plot of the $I_c\Phi$ data seen in figure 5.7. We notice a single peak in the frequency domain and white noise at higher frequencies, so a low-pass filter routine was found appropriate and was implemented to obtain the single-junction diffraction pattern. In figure 5.9c we show a schematic of representation of how a corner junction can exhibit SQUID-like modulations. A broken barrier can create two very asymmetric junctions working as a SQUID. It is the asymmetrical geometry what makes the SQUID oscillations just a perturbation of the bigger single-junction diffraction pattern.

However, we also encountered diffraction pattern data where more than 1 SQUID geometries were formed in a single junction contact. In these cases, multiple peaks in the FFT plot could be discerned, corresponding to the different SQUID areas. Figure 5.4 is an example of a dominant Josephson junction forming a diffraction pattern that is modulated by SQUID oscillations. Figure 5.10 shows the diffraction pattern data and the filtered data using a notch filter based on the 2 peaks that could be isolated in the FFT plot. Figure 5.11 shows the same type of analysis but now done to a corner junction $I_c\Phi$ plot. We can clearly see the 2 SQUID area peaks in the FFT plot indicating the frequencies to be used in out notch filter routine.
Figure 5.9: FFT plot and $I_c \Phi$ data showing a peak corresponding to the SQUID oscillation period. We cannot see any more discernible peaks at higher frequencies, so for our data analysis, a low-pass filter with roll off frequency of 250 $\text{A}^{-1}$ was used to obtain the underlying single-junction diffraction pattern. The schematic view of the corner junction shows a broken barrier creating a split junction case.
Figure 5.10: Notch filter applied to $I_c \Phi$ plot of edge junction as seen in figure 5.4. Notice the 2 SQUID areas indicating at least 3 Josephson junctions in the same contact. Although a higher frequency peak is also observed, its magnitude is much smaller than that of the 2 main SQUID peaks and its contribution to the overall noise level of the plot is very small. A notch filter spanning the 2 main SQUID areas was applied to see the underlying single-junction diffraction pattern.

Figure 5.11: Notch filter applied to $I_c \Phi$ plot of corner junction and FFT data showing SQUID areas. Notice the 2 SQUID areas indicating at least 3 Josephson junctions in the same contact. A notch filter spanning the 2 frequencies was applied to see the underlying single-junction diffraction pattern.
We can see multiple peaks in the FFT plot at different frequency ranges and with amplitudes rivaling the behavior of low-frequency modulations. A low-pass filter was used to exhibit the underlying single-junction behavior.

In this same path of junction characterization, we encountered cases in which $I_c\Phi$ plots showed oscillatory behavior in several different frequency ranges with amplitudes that competed with the underlying single-junction behavior. In extreme cases, these devices behaved like SQUIDS completely and no single-junction behavior could be isolated. Figure 5.12 shows a $V\Phi$ plot of an edge junction and the corresponding FFT analysis. One can see that the amplitude of several of the SQUID oscillations are now comparable to the amplitude of the low-frequency single-junction diffraction pattern. Fortunately, due to the sharpness of the SQUID oscillation, a low-pass filter still allowed us to recover the edge-junction characteristic behavior.

In figure 5.13 we see the extreme case of a junction being split into several SQUID areas tunneling in parallel. Figures 5.13a and 5.13c show the $V\Phi$ plot of the same junction but different field current ranges. We can see oscillatory behavior in high frequencies as well as amplitude modulation in the form of beats indicating SQUIDS with similar frequencies interfering with each other. Nevertheless, we can also find a low frequency envelope that indicates that a SQUID with 2 junctions with similar characteristics are predominant. Unfortunately, we have no control on the actual position of these multiple junctions within the fabricated structure, thus we were not able to tune this behavior for our benefit.

To summarize this section, our efforts towards a reproducible use of Josephson junctions in edge/corner geometries allowed us to see two distinct behaviors in the shape of the measured $I_c\Phi$ patterns indicating that Ba122 crystals manifest an anisotropic gap that is s-wave in nature. However, the extent of our results was hampered by the lack of a protocol that yielded the consistent surface properties on the Ba122 crystals.
Figure 5.13: Single edge junction behaving as a SQUID. We can see multiple peaks in the FFT plot at different frequency ranges and with amplitudes rivaling the behavior of low-frequency modulations. A low-pass filter was used to exhibit the underlying single-junction behavior.
that we require for further analysis. Thus, we decided to change our approach towards this problem in favor of an experiment that didn’t rely on clean surfaces perpendicular to the c-axis of our crystals and on the mechanical abrasion needed to obtain them.

### 5.2 Proximity-induced signatures of $s\pm$ superconductivity

After attempting to probe the pairing symmetry of Ba122 crystals through Josephson interferometry, we decided to switch our approach to this problem to an experiment with more potential to discern between individual extended $s$-wave pairing models, now that we understand that $d$-wave superconductivity has been ruled out from the list of candidate models for the Ba122 system. For this reason we switched to the measurement of the proximity effect of a FeSC on an $s$-wave superconductor and, in particular, how the former alters the DOS spectrum of the latter. Section 4.1.2 covers our fabrication protocols, and once we settled on doing these measurements on optimally Co-doped Ba122 crystals from Paul Canfield, we proceeded to measure the differential conductance, which we know that is proportional to the DOS of the superconductors in the structure.

From the theoretical background in section 3.2, we know that the proximity effect of an $s\pm$ superconductor on an $s$-wave superconductor with a smaller average gap $\Delta_s$ depends on a bulk coupling constant $\gamma_\alpha$ and an interface coupling constant $\gamma_{B,\alpha}$ (see equations 3.16 and 3.17). In summary, $\gamma_\alpha$ determines which $s\pm$ gap $\Delta_\alpha$ will be favored for an alignment with the $s$-wave gap $\Delta_s$, but the magnitude of the effect the $s\pm$ gap has on the DOS of the $s$-wave superconductor is dependent to $1/\gamma_{B,\alpha}$. Taking this position, we can classify our data depending on the strength of the alignment between the conventional and the multiband superconductor and the net positive/negative proximity-induced effects on the DOS of the former.

With this in mind, we first show examples of devices where the DOS of the $s$-wave superconductor is affected by the extremes in interface transparency: when the transparency is very high, we see geometrical artifacts due to quasiparticle bound states in the Al film; for the cases of very low interface transparency, the DOS spectra shows minimal evidence of being aligned with any of the $s\pm$ gaps. These examples are equivalent to SIS tunnel junctions fabricated directly on an inert substrate. We follow our data exposition by exploring the cases where, we believe, the $s$-wave superconductor shows a partial or intermittent alignment with an $s\pm$ gap and we discuss some possible scenarios that could yield these particular results, including the possibility of Two-Level System (TLS) characteristics. Finally we present the data sets where an alignment between superconducting gaps is very likely, but the net proximity effect can be either positive or negative, resulting in different types of fluctuations in the measured DOS spectrum. In order to characterize the
type of proximity effect on the $s$-wave superconductor, we look at the $s$-wave gap markers in the tunneling spectrum; having an SIS type of tunnel junction, we expect large structures at energies $\varepsilon V = \pm 2\Delta_s$, which, for 2 Aluminum $s$-wave contacts, amounts to $2\Delta_{Al} = 380\mu V$ giving us a total spacing between the gap peaks of $4\Delta_{Al} = 760\mu V$. Since one of the Al electrodes will be insulated from the FeSC, we expect any digressions from this value to be due to an enhancement or a suppression of $\Delta_s$ due to the proximity of the $s\pm$ superconductor.

On a final note, although we tried to keep all of our devices in the classical tunneling regime to ease the biasing into higher energies\(^2\), the actual value of $R_N$ for each device is hard to predict because the growth of a tunneling barrier between Al electrodes can be affected by the roughness of the crystal on which the device is built. Thus, some devices exhibit high resistances but others show supercurrents. Regardless of the tunneling regime we face, it is worth commenting that the fluctuations in the quasiparticle region of the DOS spectrum should not be sensitive to this factor.

In the following sections I will be presenting data from 17 different samples. All of the devices were fabricated using the same nominal parameters, however we saw that each single device had a characteristic behavior of its own and could only be classified in one out of four general regimes: Strong coupling states (high interface transparency), minimal coupling states (low interface transparency), partial or intermittent alignment states (weak coupling with TLS behavior) and aligned states (weak coupling with negative/positive proximity effects). We numbered our samples according to this list and in table 5.1 we present the sample number, figure number and characterization regime.

\(^2\) SIS tunneling devices that show a supercurrent $I_c \approx 1\mu A$ with areas similar to those of our devices have values for $R_N \approx 100\Omega$, which forces us to apply 10’s to 100’s $\mu A$ to achieve the right levels of biasing. Heating effects due to the large currents decrease our signal to noise ratio.
## 5.2.1 Strong coupling (Geometrical artifacts)

We start the exploration of the different coupling regimes by starting with the extremes. In first instance we will look at the case where the interface transparency is very large and the $s$-wave superconductor is in a strong coupling regime with the Ba122 crystal. In this scenario, we see the existence of other mechanisms that create irregularities that could mask our results but are unrelated to the proximity-induced changes that an $s\pm$ superconductor can produce on the $s$-wave superconductor next to it. In particular, let's look at the $dI/dV$ curve shown in figure 5.14, where we see the differential conductance spectrum of a device that shows gap suppression and several peaks and resonances at energies from $1mV$ to $7mV$.

T. Wolfram [63] showed in a publication in 1968 that the occurrence of periodic oscillations in the single mV range of DOS measurements (known as Tomasch oscillations) can be explained through BCS given a special geometrical arrangement of superconducting materials. The proposed geometry is a heterostructure where a thin film of a superconductor (S1) ($d < \xi$) is placed next to a thick superconductor (S2) with an average gap $\Delta_2 >> \Delta_1$. Quasiparticles injected in S1 reach the interface with S2 and notice a strong spatial variation in the electron-electron interaction. This abrupt change turns the interface into a barrier that reflects the quasiparticles back into S1 in a degenerate state. For cases where the mean free path in S1 is very large ($l \rightarrow \infty$), the interference between incident and reflected quasiparticles is expected to form bound eigenstates which result in the resonances found in the differential conductance plots at energies $E < \Delta_2$.

By looking at figure 5.14a, we see that the resonances end at $\sim 7mV$, which is consistent with the energy of

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<td>Strong coupling</td>
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Table 5.1: Classification of samples depending on net proximity effect.
Figure 5.14: Sample 01 - Differential conductance of device showing several peaks at energies between 1mV and 7mV. Notice the gap suppression in figure 5.14b. Figure 5.14c shows a linear fit to the peak position. Inset in dI/dV graph shows corresponding IV curve.
one of the accepted gaps in Co-doped Ba122 superconductors.

Some of the curves to be presented show indication of Tomasch oscillations for energies $V < 10mV$, so attention was placed in separating these geometrical resonances from perturbations due to proximity-induced changes in the DOS of Al films by looking at the relation shown in figure 5.14c; peaks due to Tomasch oscillations happen at energies corresponding to multiples of a fundamental frequency $\omega$ and, thus, adjust themselves to a linear fit in an energy vs peak number graph. Proximity-induced conductance fluctuations do not abide to this restriction, so they can be picked out a linear fit plot.

### 5.2.2 Minimal coupling regime

In our fabrication procedures, one of our major goals was trying to understand the sensitivity of the coupling constants determining the proximity effect to the different environmental variables faced during the assembly of the tunnel devices. Some of the structures we measured show a very small indication of changes in their superconducting characteristics due to the presence of the Ba122 crystal. Figures 5.15, 5.16 and 5.17 are examples of these types of devices. We measured the differential conductance spectrum of these devices up to bias voltages of $V_{bias} \sim 20mV$ (above the highest expected value of $\Delta_{s\pm}$) and noticed that the spectrum had the same profile as a regular SIS tunnel junction without any crystal. Figure 5.15 shows an example of this behavior. We notice the flat conductance above the gap markers and only a very slight deviation on the spacing between gap peaks from the accepted bulk value.

Figures 5.16 and 5.17 show a small deviation on the previous behavior in that the gaps are slightly enhanced. The device in figure 5.16 shows a flat differential conductance profile outside the gap structures, however in figure 5.17 we can see a small perturbation in the $dI/dV$ curve at a bias voltage of 8.6$mV$. No other features could be observed at higher bias voltages.

The profiles seen in figures 5.16b and 5.17b could indicate actual proximity coupling to the Ba122 crystal, but a high opacity in the interface between the s± and the Al film could result in DOS perturbations that are too small to be measurable. Thus, we conclude that during the fabrication a very thick dead layer developed on the Ba122 crystal effectively reducing its effect on the Al film that was deposited on it.
Figure 5.15: Sample 02 - Differential conductance of SIS tunneling device with minimal proximity-induced changes. We notice a small change in the expected gap feature separations and we measured a flat profile in the DOS spectrum at higher bias. Inset shows corresponding IV curve.

Figure 5.16: Sample 03 - Differential conductance of SIS tunneling device with minimal proximity-induced changes. We notice a small change in the expected gap feature separations and we measured no changes in the DOS spectrum at higher bias. Inset shows corresponding IV curve.
Figure 5.17: Sample 04 - Differential conductance of SIS tunneling device with minimal proximity-induced changes. We can see a slight enhancement in the gap separation energy and a small feature in the plot 5.17c which could be proximity-induced, however the signal-to-noise ratio was not large enough for further analysis. Inset shows corresponding IV curve.
5.2.3 Partial/Intermittent gap alignment regime

Our measurements on SIS tunnel junctions yielded a variety of results that show an anomalous change in the differential conductance spectrum at energies greater than 3mV. This change can be exemplified by the dI/dV spectrum shown in figures 5.18 and subsequent. First of all, we notice a deviation from the signatures seen in section 5.2.2 by a generalized monotonic climb in the differential conductance for increased |Vbias|, which indicates the presence of a stronger superconductor in proximity. This asseveration gets confirmed by the significant change in the energy profile of the s-wave gap structures. The dI/dV data shows a sudden increase in the measured noise which gets reversed during the retrace phase in the measurement and is characterized by a triggering bias voltage Vbias ∼ 3.3mV. The signal-to-noise ratio in these devices seems to be resilient to improvement through averaging and passive filtering, indicating that there are dynamical effects related to the coupling of the Al film to the FeSC different from white noise.

Using a spectrum analyzer, we looked at the Power Spectral Density (PSD) as a function of frequency for different values of DC bias voltage. Figures 5.18c and 5.18d show the compiled set of PSD curves as for positive and negative bias regimes. The dashed line shows a region that divides two distinct noise regimes that happen when the bias voltage is ∼ 3mV. No particular peaks are appreciable in the frequency range used for the measurement (aside from the 60 Hz noise and higher harmonics) but two defining features can be identified: we can see a transition into a higher noise floor that shows a PSD decaying faster than the 1/f characteristic curve and, for Vbias ∼ 3.5mV and Vbias ∼ 5mV, we see Lorentzian profiles in the noise spectrum, indicating the existence of a TLS. The curves showing this behavior are marked in bold in each of the figures. It is important to notice that the Lorentzian profiles are present only for particular bias points coincidental with the gap energies in the Ba122 crystal telling us that there is a switching dynamic in the alignment of Δs with the characteristic Ba122 gap for the given bias point.

Figure 5.19 shows another example of a device exhibiting an abrupt change in the signal-to-noise ratio at a bias voltage of 3.3mV. The similarities between the devices can be summarized in the following way: we can identify a slight decrease in the gap magnitude of the Al electrode (figures 5.18b and 5.19b); there is an increase in the differential conductance as a function of the magnitude of the applied bias voltage and, finally, a switch into an elevated noise region at Vbias ∼ 3.3mV.

An interesting set of examples of devices showing a bias-dependent noise floor can be seen in figures 5.20 and 5.21. Here we notice that the nature of the coupling between the Al film and the Ba122 crystal is different for both devices: the device in 5.20b exhibits a large enhancement in the gap feature separation and a flat conductance outside them, however the device in 5.21b shows a slight gap suppression and a bias-voltage dependence of the conductance. However, in both cases a significant change in the dI/dV spectrum
Figure 5.18: Sample 05 - Differential conductance plot of SIS tunnel device showing negative proximity coupling and a noise onset. Figures 5.18c and 5.18d show the PSD spectra indicating a distinct offset in the noise floor as a function of $V_{bias}$. We can see through the curves in bold colors the transition into a higher noise floor and the energies on which a Lorentzian profile is present. Inset in the dI/dV graph shows corresponding IV curve.
Figure 5.19: Sample 06 - Differential conductance plot of SIS tunnel device showing negative proximity coupling and a noise onset. We notice a small change in the expected gap feature separations and a monotonically increasing characteristic conductance with increased $|V_{bias}|$. Inset shows corresponding IV curve.

happens for bias levels of $6.5mV < V_{bias} < 8mV$. These fluctuations seem to be part of the noise-generating dynamics that are bias dependent in that they either disappear or show a telegraph-type switching within a trace/retrace scan or between consecutive scans. Figures 5.20c and 5.21c show trace irregularities with similar characteristics in the same energy range. For one case, the conductance changes behavior between scans whereas for the second device, the conductance changes between a trace and the retrace. Both features are significantly larger than the noise levels and happen over large averaging times.

The behavior just described seems consistent, at least as a first approximation, with a scenario where our SIS tunnel junction sits at a boundary between 2 order parameter domains. A large phase difference between the two equivalent $s\pm$ gaps with the same coupling constants and magnitudes could produce a switching behavior in the phase alignment of the Al gap with them. This scenario explains the energy ranges on which the noise floor in our measurement suddenly increases and the instability of the $8mV$ fluctuations over time.

In figure 5.22 we see that a TLS is established in the Al film when the alignment with $\Delta_1$ on either side of the domain wall is equally likely.
(a) dI/dV curve showing full spectrum. 

(b) Low $V_{\text{bias}}$ dI/dV plot showing gap magnitude. $4\Delta_A$, in blue for comparison.

(c) Small feature in conductance spectrum from figure 5.17a.

Figure 5.20: Sample 07 - Differential conductance of SIS tunnel device showing proximity coupling and a noise onset and intermittent conductance fluctuations at higher bias. Inset shows corresponding IV curve.
(a) $\frac{dI}{dV}$ curve showing full spectrum.  
(b) Low $V_{\text{bias}}$ $\frac{dI}{dV}$ plot. $4\Delta_{Al}$ in blue for comparison.  
(c) Small feature in conductance spectrum from figure 5.17a.

Figure 5.21: Sample 08 - Differential conductance plot of SIS tunnel device showing proximity coupling and a noise onset and intermittent conductance fluctuations at higher bias. Inset shows corresponding IV curve.
Figure 5.22: Diagram of Al film on an order parameter domain boundary of a Ba122 crystal. Across the domain wall, a finite constant phase difference can be defined between equivalent gaps $\Delta_1$ and $\Delta_2$ but coupling constants remain the same. The $s$-wave superconductor enters a degenerate state where alignment with $\Delta_1$ of either domain is equally likely, creating an effective TLS. The switching behavior is seen in the differential conductance spectra.

### 5.2.4 Aligned gap regime

In this section we will review the characteristic differential conductance spectra for devices where an Al film has distinct signatures of proximity-induced enhancements/suppressions; these induced effects would be seen through changes in the $s$-wave gap markers and the presence of perturbations in the conductance baselines that cannot be attributed to geometrical resonances. We first look at measurements showing devices with a significantly suppressed gap, indicating a negative proximity effect, and structures at singular energies in the Al conductance spectrum that are consistent with gap magnitudes in an $s\pm$ superconductor from the literature. Finally, we present examples of devices where a positive proximity effect is identified. In particular we see features in the $dI/dV$ spectrum that adjust well to the predictions seen in chapter 3.

**Negative Proximity effect**

For the devices we identified as being under a negative proximity effect, we first look at differential conductance spectra where the gap markers show significant suppression, albeit no particular fluctuations could be measured at higher bias voltages. First we see figures 5.23 and 5.24 which show the behavior of devices with an appreciable gap suppression and a particularly steep increase in conductance for bias voltages away from the gap markers. In 5.23a we see a symmetrical 2-fold enhancement in the conductance for a change in the bias voltage of $4mV$ in both positive and negative bias regimes. On the other way, in 5.24a we notice an asymmetrical enhancement in conductance with a saturation point in the positive bias regime at around $7mV$ but no similar effect in the negative bias regime.
Figure 5.23: Sample 09 - Differential conductance plots of SIS device showing a negative proximity effect. We notice an abruptly increasing conductance profile with increased bias voltage. Inset shows corresponding IV curve.

Figure 5.24: Sample 10 - Differential conductance plots of SIS tunneling device showing a negative proximity effect. We notice a high asymmetry in the conductance profile with increased bias but no localized fluctuations with an amplitude larger than the noise floor. Inset shows corresponding IV curve.
Lastly in this category, we see in figure 5.25 a device that shows modulations around the gap feature. Taking only the smallest peaks in conductance, the spacing between these markers is only of $450\mu V$, however the second set of peaks sit with a spacing of $850\mu V$, representing almost a 2-fold change. Outside this region, we also notice a monotonic increase in conductance with no saturation point in our measurement range.

The next step in our analysis look at devices that show a negative proximity effect with the addition of conductance peaks or dips at bias voltages away from the central $s$-wave gap markers. Figure 5.26 exemplifies this behavior. In the same way as with the devices shown in figures 5.23 and 5.24, we notice a significantly suppressed gap and a monotonically increasing conductance as a function of $|V_{bias}|$. However, when our bias voltage scans around the $\pm 7mV$, $\pm 11mV$ and $\pm 15mV$ we notice well-defined dips in the conductance baseline that remain consistent over repeated measurements. Looking back at the curves in section 5.2.3, we notice that the switching dips in conductance happen in the same bias range as with the fluctuations seen in figure 5.26c.

We then proceeded to analyze the temperature dependence of the conductance dips seen in figure 5.26 to see if the magnitude of the superconducting gap of the Al film was tied to them. Figure 5.27 summarizes this analysis. We repeated the differential conductance spectrum measurement in a range of temperatures from $320mK$ to $1.1K$, as seen in 5.27a, focusing on the conductance dips. The bias voltage at which these dips appear decreases with increased temperature. We took the normalized bias voltage of appearance, plotted it against the system temperature and fitted the resulting scatter graph with an expression for the BCS gap of an $s$-wave superconductor. Figure 5.27c shows a very close agreement for most conductance dips for a fit.
Figure 5.26: Sample 12 - Differential conductance spectrum of SIS tunnel junction showing a negative proximity effect and dips in conductance at several bias voltages. Figures 5.26a and 5.26b show the gap features indicating a negative proximity effect. Figures 5.26c, 5.26d and 5.26e show the quasi-symmetrical feature profiles at $\pm 7.2\, mV$, $\pm 11\, mV$ and $\pm 15.5\, mV$ respectively. We also notice a general monotonic increase in the conductance with increased bias voltage. Inset in $dI/dV$ graphs show corresponding IV and low-bias conductance curve, respectively.
of a BCS gap with $T_c = 1.35K$. The calculated $T_c$ is higher than the accepted value of $1.2K$ for clean bulk Aluminum but seems reasonable given the proximity effect acting on the thin Al film.

Figures 5.28 and 5.29 show more examples of similarly behaving SIS tunnel devices exhibiting gap suppression and conductance dips at different values of bias voltage. Although the particular position in the bias regime where the conductance dips appear vary between the two devices, the temperature dependence of the position of the dips tracks the BCS gap of Al as revealed figures 5.28b and 5.28c. This conduct stands in agreement with the behavior of the tunnel junction shown in figures 5.27b and 5.27c. It is worth noticing that the device in figure 5.29 shows a supercurrent and a series of resonances in the low-bias regime that resemble the geometrical artifacts explored previously. Nevertheless, a pair of conductance dips appear in a biasing regime away from the above mentioned resonances and in similar positions to those seen in the other example devices in this section.

The negative proximity effect is predicted by Stanev and Koshelev as a property of $s$-wave–$s\pm$ superconductor structures, however, the temperature dependence of the conductance features does not present itself in the theoretical analysis. In addition to this, we can see that most samples that show a negative proximity effect also exhibit a conductance profile that does not saturate at low bias, as we would expect, but monotonically increases with the magnitude of the bias voltage. We are inclined to consider the possibility that devices like the previously described are in a strong coupling regime where the position of the proximity-induced perturbations in the DOS of the $s$-wave superconductor and the differential conductance profile depend on a combination of the gap magnitudes of the 2 superconductors in the fabricated heterostructure, rather than only on the magnitudes of the $s\pm$ gaps. Further theoretical work in this area may be necessary.
Figure 5.27: Sample 12 - Temperature dependence of conductance dips and gap markers from figure 5.26 and fitting to BCS amplitude of $s$-wave gap. We notice that the energy at which the conductance dips appears decreases with increased temperature, following closely the shape of the Al gap fitted to $T_c = 1.35K$.
Figure 5.28: Sample 13 - Differential conductance spectrum of SIS tunnel junction showing a negative proximity effect and dips in conductance at several bias voltages. We can see a marked suppression of the Al gap and a series of conductance dips at higher bias voltages. The temperature dependence of the position in the bias voltage axis of these dips is shown, also pointing to a behavior that tracks the BCS gap of the Al film. Inset shows corresponding IV curve.
Figure 5.29: Sample 14 - Differential conductance spectrum of SIS Josephson junction showing a negative proximity effect and dips in conductance at several bias voltages. We notice that this device shows a supercurrent and a series of resonances happening close to the gap features. Two distinct conductance dips appear at 5mV and 7mV bias regimes.
Positive Proximity effect

Finally, we now look at the differential conductance spectra of SIS tunnel devices affected by a positive proximity coupling. In these cases, we notice a clear enhancement of the Al gap, in agreement with the familiar proximity effect between 2 conventional superconductors with different gap magnitudes. In first place we will look at the devices shown in figures 5.30 and 5.31. Both of these devices exhibit a Josephson junction behavior with multiple subgap features and evidence of proximity-enhanced superconductivity. Outside the Al gap region, we see multiple resonances that can be attributed to geometrical artifacts, yet both devices show conductance fluctuations in the energy scale of interest to us that stand apart from the previously mentioned resonances.

For the device in figure 5.30, we notice a continuous set of resonances ending in a large conductance dip for $V_{bias} = 3mV$. With increased bias voltage magnitude, we see a region of diminished oscillations followed by two sets of symmetrical conductance dips at $\pm 4.75mV$ and $\pm 6.75mV$. For higher bias levels, no more conductance fluctuations can be identified. In figure 5.31, numerous features are identified as we move away from the Al gap energies, however a set of peaks at the 8$mV$ bias region stand out respect to the numerous conductance dips. All of these features are persistent for subsequent measurements.

Out of the devices we identified as affected by positive proximity coupling, the tunnel device seen in figure 5.32 shows most of the elements explored in section 3.2. First, we notice in figures 5.32a and 5.32b a significant gap enhancement but a relatively flat conductance profile outside the gap region. Yet, at a bias voltage between 5$mV$ and 8$mV$ we can clearly discern a feature that starts with a sharp conductance peak followed by a depressed conductance plateau and ending in a step function back into the baseline. There appears to be secondary structure within the plateau region, but its amplitude is smaller than that of the step function itself. Figure 5.32c shows this structure in detail where a dashed line has been added for reference representing the trace of the conductance spectrum without the perturbation. The symmetric position in the negative bias region also shows a depression in the conductance that covers a similar bias range, however the sharp peak that characterizes the structure in the positive bias is absent in the negative bias perturbation.

We took the conductance spectrum from figure 5.32a and repeated our measurements varying the sample temperature. The results from this measurements are presented in figure 5.33. We see in 5.33a and 5.33b the positive and negative bias regimes in the differential conductance spectrum with varying temperature. We notice that the most prominent structures are temperature independent, telling us that this device is under a different coupling regime than the examples exhibiting a negative proximity effect in section 5.2.4.

For the results given in this section we noticed that the presence of a Ba122 crystal can also enhance
Figure 5.30: Sample 15 - Differential conductance plot of SIS Josephson junction showing positive proximity coupling and multiple central and higher-bias fluctuations. We notice that the largest of the central features lies just outside the $4\Delta_{Al}$ spacing, while the rest of the peaks around the gap energy are much smaller in bias spacing. Conductance dips at $\sim 3\text{mV}$ are also present with no other similar structures at higher bias. Temperature dependence of the spectrum is shown. Inset shows corresponding IV curve.
Figure 5.31: Sample 16 - Differential conductance plot of SIS Josephson junction showing positive proximity coupling and multiple conductance fluctuations at all bias regimes. Inset shows corresponding IV curve.
Figure 5.32: Sample 17 - Differential conductance plot of SIS tunneling device exhibiting a positive proximity effect and marked features at higher bias voltage. We notice a step-like function consistent with the predictions seen in section 3.2 and a relatively flat conductance profile at higher bias voltage. Inset shows corresponding IV curve.
Figure 5.33: Sample 17 - Temperature dependence of the differential conductance spectrum from an SIS tunnel junction exhibiting proximity-induced features. Unlike previous devices that showed a temperature dependence of the fluctuations in the conductance spectra, the structure in this device shows a temperature-independent behavior.
the superconducting properties of the Al film that lies in proximity. This effect is closer to the expected behavior of a weak superconductor coupling with a stronger one, namely the enhancement of the weaker superconductor and the suppression of the stronger material. On a final note, it is very interesting to see that the structure examined in figure 5.32c can be compared with the predictions by Stanev and Koshelev for a proximity coupled s-wave superconductor to an s± superconductor, which are summarized in figure 3.8. It is also worth noticing that the sharpness of the perturbations in the conductance spectrum are strongly dependent on the interface coupling constants, so if the properties of our devices favor even a slight particle/hole asymmetry, they could influence the interface transparency just enough to wash out or enhance specific features in the conductance spectrum. This could explain why some of the measured fluctuations are not identical when measured in the symmetric bias regime.

5.3 Discussion

In this chapter we presented the result of our measurements on Co-doped Ba122 crystals and their implications regarding the elucidation of the pairing symmetry model that describes these materials. From the Josephson interferometry experiments, we have gathered the following information regarding Ba122 superconductors:

1. Corner and edge Josephson junctions show indications of only Fraunhofer-like diffraction patterns. The absence of double central peaks in the interferometry measurements points towards s-wave pairing.

2. Corner Josephson junctions show interference patterns consistent with an asymmetric nodeless superconducting gaps in the BZ.

3. The $I_cR_n$ data supports the idea of an effective gap in corner junctions (probing electron and hole pockets together) that is weaker than that of the central hole pockets alone (for equal $R_N$, lower $I_c$ in corner junctions), which supports an alternating sign between gaps of different nature.

Nevertheless, the requirement of a surface with reproducible properties on which to fabricate our Josephson junctions left us with only partial understanding of the gap asymmetry present in these Ba122 crystals. Through the use of proximity-induced changes in the DOS of an s-wave superconductor due to the superconducting properties of a Ba122 crystal, we expected to find specific evidence pointing towards a particular pairing model; nevertheless, what we found is that small particularities of each produced sample created devices with very broad combinations of properties. Using the coupling between the s-wave superconductor and the Ba122 crystal as our metric, we classified our results and compared them across the board. Our measurements led us to make the following conclusions about the proximity effect of Ba122 crystals on Al
1. The presence of the FeSC in proximity with a thin Al film can induce significant changes in the DOS of the latter.

2. The proximity effect not only manifests itself in terms of perturbations of the DOS baseline at energies coincidental with the FeSC superconducting gaps, but also through direct enhancement or suppression of the superconducting gap of the thin s-wave film in proximity with the FeSC. Thus we can talk about both a positive and a negative proximity effect.

3. The nature of this proximity effect seems to be extremely sensitive to the interface properties between the FeSC and the thin s-wave superconductor, resulting in devices in very different coupling regimes yielding the broad variety of conductance profiles shown in this chapter.

4. The temperature-dependence data indicates that the devices that we identified as being in a negative proximity-coupling regime also fall in a strong coupling regime, where the measured features in the DOS spectrum of the s-wave superconductor cannot be treated as results of weak perturbations of \( \Psi_s \) due to the presence of the FeSC but rather to higher order effects where the order parameters of the s-wave and the FeSC are even more closely intertwined.

The lack of devices found in consistent and/or tunable coupling regimes limits the depth of our conclusions about our proximity effect measurements, however, there is one factor that points towards s± superconductivity being responsible for the pairing properties of Ba122 superconductors; that factor is the presence of different types of proximity effects for the same crystal composition. Experiments have already characterized the multiband quality of FeSC’s and from those measurements we can see that all of the gaps in Ba122 superconductors are larger than that of the aluminum we selected as our s-wave superconductor. Thus, experience tells us that we should only expect a proximity-induced enhancement of \( \Delta_{Al} \) when placed next to a Ba122 crystal in conjunction with a suppression of \( \Delta_{\alpha,Ba122} \), given a consistent material quality. Indeed, such enhancement-only proximity effects have already been described for multiband superconductors like MgB\(_2\) by Brinkman and Golubov [56], where they show that, in an experimental arrangement similar to ours, the perturbation of the DOS spectrum of a weaker superconductor manifests itself in the form of gap enhancement and the formation of peaks at energies equivalent with the gaps of the stronger multiband superconductor.

Stanev and Koshelev explain that, applied to an s-wave–s± heterostructure, the formation of an aligned state between \( \Delta_s \) and one of the \( \Delta_{\alpha,s\pm} \) results in an anti-alignment of \( \Delta_s \) with the opposite-signed gaps in the multiband superconductor. A particular combination of coupling constants \( \gamma_{B,\alpha} \) combined with this anti-aligned state results in a frustrated state where all gaps become suppressed. By looking at our results, we can
see that most devices can be correctly categorized into either proximity-enhanced or proximity-suppressed, and it is the fact that there are two clear regimes what constitutes a signature of s± superconductivity.

Furthermore, since the gap suppression affects both $\Delta_s$ and all $\Delta_{\alpha,s,\pm}$ and it depends on the specific combination of interface coupling constants, we could explain the varying position of the observed fluctuations in the differential conductance spectra as actual measurements of the current value of some of the $\Delta_{\alpha,s,\pm}$ in different levels of suppression. Thus, by working on the fabrication protocols we could find a way to tune the actual interface coupling constants to show this particular effect.

In practice we have found that the passivation of the Ba122 surface through the deposition of a normal metal could help in tuning the coupling between an Al film and a Ba122 crystal by preventing the uncontrolled oxidation and degradation of the crystal surface. Then, by controlling the thickness of the normal metal layer and keeping a consistent crystal quality we can change the interface transparency at will. This factor could be particularly important since part of our current fabrication protocols include the curing of the adhesion agent fixing the crystal to our Si chips by the use of a hot plate. Surface passivation could protect the crystal quality even in atmospheric conditions through this mounting procedure. As of today, some attempts at surface passivation have been done through the deposition of an Ag layer through sputtering or a thin film of Pd through e-beam evaporation, but not enough data points have been taken to make a statement about the relevance of this argument.
Chapter 6

Conclusions and Future Work

The unconventional nature of Iron-based superconductivity continues to provide condensed matter physicists with a challenging system that puts our understanding of strongly-correlated materials to the test. In this document we have attempted to bring some light into the still controversial pairing symmetry problem of the Co-doped \( \text{Ba(FeAs)}_2 \) family of superconductors. As a result of continuous characterization of this material, the scientific community favors an extended \( s \) pairing model, the \( s\pm \) model, to explain the origin of the pairing mechanism in these superconductors. The \( s\pm \) model relies on the interplay of a multiband order parameter with alternating signs between different superconducting gaps to provide a medium through which Cooper pairs can be formed; however, up to this day, no definitive experimental results have fully confirmed this belief. We confronted the pairing symmetry problem in Ba122 crystals through the use of the Josephson effect and its characteristic phase sensitivity to test the validity of the \( s\pm \) model in two distinct experimental configurations.

Our first attempt was done by fabricating S-N-Ba122 Josephson junctions in various geometries and analyzing the magnetic flux dependence of their characteristic critical currents. This measurement helped us dismiss \( d \)-wave superconductivity as one of the pairing symmetry candidates and steadily pointed us towards an extended \( s \) model, of which the two more popular candidates are \( s++ \) and \( s\pm \). This experimental approach could not be more specific in its conclusions, though, due to the difficulty in obtaining clean and consistent surfaces on the Ba122 crystals, which are necessary for a reproducible device fabrication, keeping us from doing a comprehensive comparison of the results across different samples.

We then moved to an indirect test of \( s\pm \) pairing through the use of the proximity effect of Ba122 crystals on thin Aluminum films. In this experiment we tested how the presence of a stronger multiband superconductor could affect the density of states spectrum of a thin \( s \)-wave superconducting Al film. Our results showed that thin Al films can be proximity-enhanced or proximity-suppressed by the presence of a nearby Ba122 crystal. In particular, we concluded that the net proximity effect could change drastically in nature across samples due of its high sensitivity to interface conditions, which determine the net coupling between the two superconductors. Yet, although the fine tuning of the coupling constants in this system
could not be achieved, it is the existence of both positive and negative proximity effects across the measured devices the factor that gives the strongest indication of $s\pm$ pairing as the correct model to describe Ba122 superconductivity.

The common denominator in a successful use of the above mentioned experimental approaches to determine the pairing symmetry of these multiband superconductors seems to be the attainment of clean and consistent crystal surfaces for the fabrication protocols. In this regard, we hypothesize that a prompt passivation of a crystal surface with a normal metal layer upon cleaving can both arrest the degradation of the crystal under analysis and give us control of the interface transparency by exploring material options and thicknesses. An exploration of this phase space could provide the necessary tools to be able to extend our analysis across different families of FeSC’s or doping regimes.

We believe that the conjunction of the experimental techniques used in this analysis may prove extremely valuable in characterizing the pairing symmetry of other families of FeSC’s since their combination provides us with a tool that is sensitive to an extensive number of plausible pairing symmetry models. In particular, this two techniques in tandem can be used to probe controversial order parameter symmetries like the one of the KFeAs compound. In this case, a nodal gap has already been identified, but an accurate characterization of this gap as either a nodal $s$-wave or a $d$-wave is still in the air. Josephson interferometry and the search of proximity-induced signatures could provide a definite answer to this problem.

The phenomenon of iron-based superconductivity keeps bringing surprising challenges to the desks and laboratories of physicists with every new discovered family and every new measurement regime. We hope that the work presented here helps at least in a small amount in the advancement towards a more comprehensive understanding of the field of superconductivity and towards the characterization and design of more of these interesting materials.
References

[1] H. Onnes, KNAW 120b (1911).


