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Electric Transport Measurements of Thin Film High-$T_c$ Superconductor Bicrystal Grain Boundary Josephson Junctions

by

Daniel John

A Doctoral Thesis submitted in partial fulfilment to the requirements for the award of Doctor of Philosophy

in the Faculty of Science Department of Physics

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Abstract

Josephson junctions are an integral component of superconducting electronics because of their non-linear response and have not only been incorporated into a number of devices including superconducting quantum interference devices (SQUIDs) to create highly sensitive magnetometers and Josephson flux vortex transistors (JVFTs) to make fast-switching, high gain transistors but also into experiments to resolve the unexplained pairing mechanisms in high-$T_c$ superconductors.

As such, chapter 2 describes the results of an investigation into the pairing mechanism of the infinite layer superconductor $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ using a single Josephson junction. The main result of this was that observations of zero bias conductance peaks (ZBCP) strongly suggest that SLCO superconductors are $d$-wave superconductors. This also contradicts many previous reports which concluded that SLCO superconductors are $s$-wave superconductors.

Chapter 3 describes the results of measurements of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Josephson junction arrays. The results of this showed that the device had periodical behaviour at temperatures close to $T_c$ with a periodicity of 1.8 mA or 12 μT. Moreover, it was found that this device could also operate as a Josephson vortex flow transistor (JVFT) which produced gains as high as $19.28 \pm 0.03$ at 77 K. In addition, switching behaviour was also found. Therefore, the record high current gains found at 77 K and above, as well as the switching behaviour make this device highly suitable for applications as a superconducting transistor.
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1. Introduction to Superconductivity

1.1 Introduction

In 1908, Heike Kamerlingh Onnes paved the way to discovering superconductivity by firstly liquefying helium, at a temperature of 4.2K, at the University of Leiden. This meant that investigations into the behaviour of matter at low temperatures could occur below 4.2K for the first time.

At that time there were several theories regarding the electrical resistances of materials as temperatures approached absolute zero. One such theory was proposed in 1902 by Lord Kelvin. He suggested that as the temperature approached absolute zero, the energy of the conduction electrons decrease drastically, causing them to drop from the conduction band to the valence band. This would cause a minimum resistance to be seen followed by an increase in resistance with decreasing temperature.

Another theory was put forward by Dewar who proposed that the resistance would linearly decrease, until absolute zero was reached where any material would have absolutely no electrical resistance. However, Matthiessen argued that the resistance would plateau off at some finite resistance regardless of how low the temperature was because of imperfections and impurities in the lattice structure [1, 2]. These theories are shown in Figure 1.

![Figure 1: Theories of resistivity at low temperatures put forth by Dewar (black), Matthiessen (red) and Kelvin (green)](image_url)
It was not until 1911 that this debate was finally resolved when Onnes measured the resistance of mercury at low temperatures, which was used because it could be distilled to a very high purity at room temperature. The results of the experiment showed a linear decrease in resistance with temperature until 4.2 K upon which the resistance fell to zero within a few tenths of a degree. Similar behaviour was observed in lead and tin at 7.2 K and 3.7 K respectively. This effect became known as superconductivity.

It remained an obscure but intriguing effect until other institutions outside Leiden had developed the facilities needed for the production of liquid helium. After a few years, it became apparent that superconductivity was not just confined to a few pure elements but also to numerous other elements and compounds.

1.2 Fundamentals of Superconductors
Numerous fundamental parameters were found after the initial discovery of superconductivity. The first one was the critical temperature ($T_c$). Each superconducting material was found to have its own critical temperature. Above this temperature, the material is in a normal state and obeys Ohm’s law of resistance. Below this temperature, the material goes through a phase transition, into the superconducting state. An example of this can be seen in Figure 2.

![Figure 2: RT measurement of a superconductor (black) and normal metal (red). The superconductor transitions from a normal state to a superconducting state at $T_c > 0$, whereas the normal metal has a finite resistance at $T = 0$](image-url)
After the initial discovery, Kamerlingh Onnes quickly appreciated that his discovery would have implications on the production of high magnetic fields. It was well known that the flow of electrical current caused a magnetic field to arise. Thus, the winding of a wire into a solenoid created a magnet. Due to the finite resistance of the normal metals used in this application, solenoids had a tendency to burn out if a high enough current was passed through them which was caused by Joule heating. A superconductor was thought to be highly advantageous in this situation as there would be no electrical resistance and therefore no Joule heating. However, it was found that when large currents were passed through the material, the superconducting state was destroyed and the solenoids ceased to be superconducting. Thus, superconducting materials were also found to have a critical current ($I_c$).

Similarly, it was found that the application of a strong enough external magnetic field, which was used to increase current flow, also caused the breakdown of the superconducting state. This critical field ($H_c$) is dependent on $T$, with its maximum, $H_c(0)$ at $T = 0$ K. This is shown in Figure 3 and shows the range of temperatures and fields where the superconducting and normal states exist.

Another important feature of superconductors was also found in 1933 by Meissner and Ochsenfeld. The Meissner effect, shown in Figure 4, is a property of superconductors which gives them perfect diamagnetism. This is where not only magnetic fields are excluded from
entering a superconductor, but also where it expels a magnetic field from the superconductor when it is cooled below $T_c$. This means that the superconducting state is a true thermodynamic state and is not explained by perfect conductivity which would trap the flux in a normal conductor when cooled below $T_c$. If Maxwell’s equations were applied it would require that the magnetic flux inside a superconductor would not change and this would imply that the magnetic flux would remain frozen inside when cooled below $T_c$. The result of this would mean that the superconducting state is metastable rather than being in thermodynamic equilibrium. Obviously this is not the case, and in fact the superconducting material acts as a macroscopic diamagnetic atom.

![Figure 4: Behaviour of a normal conductor (left) and superconductor (right) when cooled in a magnetic field. This shows the Meissner effect displayed by superconductors when cooled below $T_c$.](image)

Moreover, it was found that when dealing with superconductors, flux had to be considered to be quantised. Flux quantisation can be explained by considering a ring of superconducting material within a bulk of normal material from which it is possible to prove that magnetic flux is quantised within a superconductor.

If a magnetic field is applied when it is in the normal state the field permeates through the material. Once the material is cooled below its $T_c$ then no supercurrents will be present at the centre of the ring, so magnetic fields can pass through. However, the supercurrents at the boundary will arrange themselves so that the total magnetic flux through the ring is quantized in units of $\Phi_0$. This is proved mathematically by
The total amount of flux can be shown to be quantised by considering a magnetic field penetrating into an arbitrarily shaped superconductor

\[ \Phi = \oint_C A \, dl = n \Phi_0 \]  \hspace{2cm} (1.1)

where

\[ \Phi_0 = \frac{\pi \hbar c}{e} = \frac{hc}{2e} = 2.07 \times 10^{-7} \text{ Gcm}^2 \]  \hspace{2cm} (1.2)

It is worth noting that \( \Phi_0 \) has a factor of \( 2e \) in it [1]. At first this was a discrepancy from London’s theory, which said that there should only be a factor of \( e \), however this was later found to be representative of the Cooper pairs that are described in the Bardeen Cooper Schrieffer (BCS) theory of superconductivity [7].

It was not until 1961 that this was experimentally viewed by two groups, one consisting of Doll and Nábauer in Munich and the other being Deaver and Fairbank at Stanford. Both measured it using extremely fine metal tubes with diameters approximately 10 μm. Doll and Nábauer used tin and lead cylinders made by condensing the metals on to a quartz fibre. Deaver and Fairbank made their tubes by electroplating tin on to a copper core. Thus, when the sample was cooled to 3.8 K, the tin became superconducting while the copper remained normal. In both cases, the magnetic field was then removed thereby creating a current by Faraday’s law. This resulted in the flux inside the cylinder remaining unchanged. A consequence of this was that the magnetic moment of the cylinder was proportional to the flux threading the cylinder. Measurements of this magnetic moment were obtained by...
situating a pair of coils at the end of the cylinders with the wire allowed to oscillate up and down between them. The magnetic moment could then be calculated from the voltage induced in the coils. Both groups found that the flux was indeed quantised as put forward by London [4].

There are two types of superconductors; type I and type II. Type I superconductors remain superconducting up to their critical field $H_{c1}$, at which point they return to their normal state. In general, these superconductors are metals such as lead and tin and are exclusively low temperature superconductors, operating in the region of liquid helium. This behaviour is noted in Figure 6.

![Figure 6: Type I superconductor characteristics, showing the critical field, coherence length and penetration depth](image)

Type II superconductors on the other hand, remain in the superconducting state until reaching $H_{c1}$ at which point it enters a mixed state, known as the Shubnikov phase. In this state, flux partially penetrates the superconductor in moderate magnetic fields. However, the bulk of the material remains superconducting. In this mixed state the material contains both superconducting and normal regions. Discrete flux lines form tubular regions, which are in a normal state, around which there is a superconducting matrix. Each tubular region is threaded by a single flux quantum and is surrounded by a vortex of persistent circulating currents which maintain the magnetic flux. It remains in this state up to $H_{c2}$, where $H_{c2}$ is much larger than $H_{c1}$. When the magnetic field exceeds $H_{c2}$, which can be many Tesla, it goes into its normal state. This behaviour is shown in Figure 7. In general, type II superconductors are
alloys such as Nb₃Sn and NbTi, cuprates such as YBCO and BSSCO, or fullerenes but also include the elements Nb, Tc, V and C. These operate at much higher temperatures, with cuprates operating well within the region of liquid nitrogen.

Another finding was by Alexei Abrikosov in 1957 [5]. He predicted that under high magnetic fields, flux would penetrate a type II superconductor in quantised tubes that typically formed hexagonal lattices. These became known as Abrikosov vortices or fluxons. Essentially, Abrikosov vortices consist of a normal core, which is proportional to the coherence length in radius, surrounded by superconducting currents which decay at a distance proportional to the penetration depth. Obviously these circulating currents induce a magnetic field, which is equal to a single flux quantum.
These were experimentally viewed in a number of experiments, and it was found that these could be pinned on defects within the crystal structure of the type II superconductor. If there were no thermal fluctuations these vortices would remain pinned indefinitely. Introducing thermal fluctuations into the system increases the Lorentz force beyond the depinning threshold allows the vortices to leave their pinning sites, allowing them to move a short distance to new pinning sites. This lowers the magnetisation of the sample to a new lower energy state and the vortices enter a viscous flow state where an electrical resistance is observed which represents the flow rate. This is called flux creep [1].

1.3 High-$T_c$ Superconductors

The 1960s and 70s brought about massive interest in the area of superconductivity, with the discovery of niobium based superconductors and the introduction of BCS theory - the first truly microscopic theory of superconducting materials - being of prime importance. In 1986, Bednorz and Muller created a new surge in activity by discovering superconductivity in the cuprate LaBa$_2$Cu$_3$O$_7$ at a temperature of 30 K [8], resulting in the awarding of the 1987 Nobel prize for physics. Up to this point the highest $T_c$ recorded was 23.1 K for Nb$_3$Ge and it was thought that superconductivity was unlikely to occur much above 25 K. Upon receiving the news that superconductivity had been discovered in an insulating cuprate, several other groups began work, replacing Ba with Sr which provided a further increase in $T_c$.

Recent work in high-$T_c$ superconductors has been based on a number of different areas. This includes further work on cuprates and the investigation of new groups of superconductors such as ferropnictides and organic superconductors (primarily fullerenes). Recent work in the field of cuprates has provided further increases in $T_c$ with the compound YBa$_2$Cu$_3$O$_7$ [9] at 93 K and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ (BSCCO-2223) at 105 K [10-12]. These were important milestones as they were the first materials to be superconductive above the boiling point of liquid nitrogen at 77 K. From these compounds further work was carried out by adding Tl to create TlBaCaCuO with cation numbers 2201, 2212, 2223 and 1234 that had $T_c$s of 80 K, 110 K, 120 K and 122 K respectively [13, 14]. By replacing Tl with Hg another increase in $T_c$ was produced. As of 2009 the highest $T_c$ for a cuprate recorded at ambient pressure is that of HgBa$_2$Ca$_2$Cu$_3$O$_8$ at 134 K [15].
Of particular interest to the experiment described in the appendix is the work conducted on GdBaCuO (GBCO) systems. GBCO was found by substituting Y for Gd and has well documented properties. This makes it an ideal material to measure to calibrate the instruments used and gain experience using the cryostat. These systems have various cation numbers including 123 and 211 which had \( T_c \)s around 92 K and \( j_c \)s up to 4 MA·cm\(^{-2}\) [16] respectively. Work has also been conducted to enhance the \( j_c \) of the samples by introducing pinning centres, such as Au nanorods and other methods of fabrication [17].

Ferropnictide compounds have also been researched thoroughly in the past couple of years since their discovery in 2006 because these compounds are very different to the cuprates, which may lead to a theory for high-\( T_c \) materials [18-22]. Fullerenes have also been found to be superconductive. These are molecules composed entirely of C in the form of hollow tubes or spheres [23-26].

However, a theory which fully describes high-\( T_c \) superconductivity has not been as easily forthcoming, unlike low \( T_c \) materials [4, 7]. At present there are numerous theories though currently no individual theory has been able to fully explain all the effects found in high-\( T_c \) superconductors.

1.4 Josephson Effect
1.4.1 Theory of Josephson Junctions
The Josephson Effect was first predicted by Brian Josephson in 1962. It was hypothesized that quantum tunnelling of superconducting electrons should occur between two weakly coupled superconductors, creating a junction [27]. The superconductors can be ‘weakly coupled’ using number of different techniques but usually can be classified as SIS, SNS or ScS, where S, I, N, c represent superconductor, insulator, normal and constriction respectively. In effect this meant that a DC current would be observed without the need for a voltage to be applied across the junction.

Instead the current is observed because of the difference in phase of the wavefunctions of the Cooper pairs across the junction. A single wave function can describe macroscopically each superconductor because each Cooper pair can be considered a boson, and thus all Cooper
pairs will occupy the same quantum state with the same energy. Mathematically this current is described by

\[ I = I_c \sin \psi(t) \quad (1.3) \]

where

\[ \psi(t) = \psi_2 - \psi_1 - \frac{2\pi}{\Phi_0} \int_1^2 A \, dl \quad (1.4) \]

In addition, if a DC voltage were applied across the junction it would cause the phase difference to evolve over time according to

\[ \frac{\partial \varphi}{\partial t} = \frac{2eV(t)}{\hbar} \quad (1.5) \]

It would also cause an AC current to flow with frequency

\[ \omega = \frac{2eV}{\hbar} \quad (1.6) \]

Thus, the quantum energy of the Cooper pairs is \( h\omega \).

The RSCJ model, proposed by Stewart and McCumber, is a very simple, macroscopic model which describes the current characteristics and dynamics of Josephson junctions with some degree of accuracy [1] using classical components.
In a magnetic field applied parallel to the junction plane the Josephson critical current has a Fraunhofer dependence as shown in Figure 10.

By assuming the current \( I \), applied to a Josephson junction, is smaller than the critical current \( I_c \) and is time dependant we can also say that the voltage \( V(t) \) is not equal to zero. However, at finite voltages quasiparticles also flow through the junction creating a current \( I_q \). Generally...
this is highly dependent on the voltage $V$ but at low voltages it is linearly governed by Ohm’s law. There is also a finite capacitance, especially for those junctions with geometry similar to a plate capacitor. This capacitance can be described as the displacement current $I_d$ where

$$I_d = C \frac{dV}{dt}$$  \hspace{1cm} (1.7)

From this the total current is given by

$$I = I_f + I_q + I_d = I_c \sin \varphi + \frac{V}{R} + C \frac{dV}{dt}$$  \hspace{1cm} (1.8)

By considering this equation with a nonlinear relation for $I_q$ we can see that this becomes

$$I = I_c \sin \varphi + \frac{\Phi_0}{2\pi R} \frac{d\varphi}{dt} + \frac{C \Phi_0}{2\pi} \frac{d^2 \varphi}{dt^2}$$ \hspace{1cm} (1.9)

It can be seen that this equation is analogous to that of a pendulum system

$$M = mg \sin \varphi + \Gamma \frac{d\varphi}{dt} + \Theta \frac{d^2 \varphi}{dt^2}$$ \hspace{1cm} (1.10)

where $mg \sin \varphi$ is the restoring torque of the pendulum, $\Gamma \frac{d\varphi}{dt}$ is the damping coefficient of the system and $\Theta \frac{d^2 \varphi}{dt^2}$ describes the moment of inertia of the system. Because of this it is often more useful to envisage whole systems of coupled pendulums in place of the full microscopic model without the need for the transport characteristics across the barrier. As with pendulum systems, Josephson junctions can be over-damped and under-damped. Using units of current in terms of $I_c$, voltage $V_c$ in terms of $I_c R$ and units of time $t$ in terms of $\Phi_0/2\pi I_c R$. This reduces equation 1.31 to

$$I = \sin \varphi + \frac{d\varphi}{dt} + \beta_c \frac{d^2 \varphi}{dt^2}$$ \hspace{1cm} (1.11)
where
\[
\beta_c = \frac{2\pi I_c R^2 C}{\Phi_0}
\] (1.12)

and is material dependent. This is known as the Stewart-McCumber parameter and explains
the hysteresis in IV plots of under- and over-damped junctions. When a Josephson junction is
under damped $\beta_c > 1$ and when it is overdamped $\beta_c < 1$ [1].

When a Josephson junction is irradiated with microwave radiation it will cause an alternating
current across the junction. This can be modelled using the RSCJ model by simply adding an
additional factor $I_{ac} \cos(2\pi f_{ac} t)$ where $f_{ac}$ is the frequency of the incident radiation. This
implies we are now dealing with a driven pendulum system. For a real pendulum, the
pendulum can adjust its eigenfrequency to that of the external drive frequency.

In the instance of a rotating pendulum this becomes highly important. The pendulum will
rotate with the driving frequency $f_{ac}$ giving a constant average velocity. In terms of Josephson
junctions this means that there is current interval where there will be a constant voltage. From
the second Josephson equation
\[
\frac{d\varphi}{dt} = 2\pi f = 2\pi f_{ac} = \frac{2\pi V}{\Phi_0}
\] (1.13)
thus,

\[ V = f_{ac} \Phi_0 \] (1.14)

and

\[ V_n = n f_{ac} \Phi_0 \] (1.15)

This implies that there will be steps of constant voltage, called Shapiro steps. These steps are caused by the superposition of the AC Josephson current and the microwave field. Each time the frequency of the AC Josephson current corresponds to an integer multiple of the microwave frequency the superposition produces an additional DC Josephson current. Moreover, the value of the current step \( I_{shapiro} \) is

\[ I_{shapiro} = 2I_c \left| J_n \left( \frac{2eV_{rf}}{\hbar \omega_{rf}} \right) \right| \] (1.16)

where \( J_n \) is the \( n^{th} \) Bessel function.

Alternatively, this system can be modelled by a mass moving down an undulating incline plane also known as the “washboard potential”. This will lead to the same equations of motion described above as long as the mass remains in contact with the plane.
Another feature found in current-voltage characteristics of Josephson junctions are so-called Fiske steps. These form at small voltages under static magnetic fields and are a result of the geometry of the junction which can be modelled as a resonating cavity. At suitable voltages and fields, the Josephson oscillations exactly fit a cavity mode of the junction creating the Fiske step. In small junctions, where the junction size is smaller than the Josephson penetration depth $\lambda_J$

$$\lambda_J = \left( \frac{\Phi_0}{2\pi \mu_0 d f_c} \right)^{\frac{1}{2}}$$

the voltage of the $n^{th}$ Fiske step $V_n$ is given by the equation

$$V_n = \frac{h n \bar{c}}{4 e W}$$

where $\bar{c}$ is the Swihart velocity, $h$ is Planck’s constant, $n$ is the $n^{th}$ Fiske step and $W$ is the width of the junction. These steps have been seen in planar junctions, Josephson junction arrays, intrinsic BSCCO junctions and YBCO bicrystal junctions to name but a few.

Another feature of the Josephson effect is that in long Josephson junctions, vortices of supercurrent are produced. These supercurrents circulate around the centre of the vortex which is situated at the junction barrier but unlike Abrikosov vortices, Josephson vortices do
not have normal cores. These circulating supercurrents also create a magnetic field equal to a single flux quantum in the same way as an Abrikosov vortex does. Moreover, it was demonstrated a propagating Josephson vortex can initiate further Josephson vortices.

1.4.2 Fabrication Methods of Josephson Junctions
The first generation of Josephson junctions employed single crystals as thin films could at that stage not be relied upon. Using these single crystal break junctions, where a single crystal is broken in two, or point contact, where one electrode is a sharp tip, the order parameter and energy gap of YBCO were found [28].

Grain boundary junctions use thin films deposited on substrates to take advantage of the difference in orientation in grain boundaries to give a significant drop in the critical current and creating the weak coupling between the two superconductors. There are several methods for forming a grain boundary junction which include bicrystal, biepitaxial and step types, some of which are shown in Figure 13. All types use the differing orientation of two grain boundaries to create the junction and are made either by growing a thin film on bicrystalline substrates such as MgO and SrTiO$_3$ or by growing the film on structured templates and relying on the changes in orientation induced by the growth. They can also be made by growing the film over a step fashioned out of the substrate. This structure and all of its properties will depend almost entirely on the morphology of the underlying substrate. However, reproducibility remains a key problem for these junctions [28].
Junctions can also be formed using artificial barriers. These junctions can be made with either single crystals or using thin films, and consists of a superconducting electrode, then a barrier which is either a normal metal or an insulator followed by another superconducting electrode. However, one of the most common methods, especially when fabricating experimental devices, uses bicrystals or in some cases tri- or tetra- crystal to create a junction. In this case, the grain boundary of each abutting crystal acts as an insulator in an SIS junction.

Each junction is characterised by its twist and tilt components of the misorientation. The tilt of the junction refers to the rotation around an axis in the plane of the substrate, whereas twist refers to the rotation around an axis perpendicular to the plane. They are distinguished further by either being symmetric, where each crystal has the same misorientation angle, or asymmetric about the grain boundary, where the misorientation angle differs. There are also 90° boundaries, which are commonly found in step-edge junctions and boundaries formed as a result of translation between the two grains. For YBCO, this boundary usually extends in the [001] direction and result in a shift of 1/3 or 2/3 of the [001] lattice vector. The grain boundary misorientation is formed by dislocations which are separated by lattice regions that are well matched. This can result in multiple sets of edge dislocations, which are dependent on the geometry of the boundary. Using standard grain boundary theory, the distance between dislocations of the same set is given by

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**Figure 13:** Example junctions formed using superconducting (S), normal (N) and insulating (I) materials.
\[ d = \frac{|b|}{\sin \theta} \]  

(1.19)

where \( |b| \) is the magnitude of the Burgers vector and \( \theta \) is the angle of misorientation. The formation of dislocations at the grain boundary is a consequence of topology rather than being dependent on the material.

Bicrystal technology uses an epitaxially grown film on top of a substrate with the desired misorientation. Since the film is epitaxially grown, the substrate grain boundary is replicated in the film and allows one to easily fabricate junctions with many different orientations. This technique has also been used to fabricate tri-, tetra- and poly-crystalline samples [29-32].

Bipitaxial samples, shown in Figure 14, are similar to bicrystal samples but use changes in the orientation caused by epitaxial growth on structured template layers and allow the position of the grain boundary to be freely selected. By choosing suitable template layers the high-\( T_c \) films are rotated in plane [33, 34].

![Figure 14: Bipitaxial junction showing the STO substrate, MgO buffer layer and YBCO thin film [35]](image)

Another form of grain boundary junctions is step-edge junctions. These are created by growing a film over a suitable step pattern. These create two grain boundaries, one at the bottom of the step and one at the top which are in series. As steps are easily created using standard photolithographic, they can be placed anywhere on the substrate surface. However, it is vital to observe some design parameters. Firstly, the step has to be larger than the film thickness. The step angle also has to be controlled because it determines the grain boundary
configuration. Typical values for this range from 50° to 60°. The substrate material is also important since it can determine the orientation of film growth.

No matter the type of grain boundary junction used, all display highly correlated relationships between the critical current density $j_c$ and the angle of misorientation $\theta$. Measurements of thin films showed a significant decrease in $j_c$ as the rotation became more pronounced, with bicrystalline junctions showing a near exponential dependence. Comparisons of symmetric and asymmetric samples with the same misorientation showed that the $j_c$ for the symmetric samples were slightly larger than those found for the asymmetric samples.

![Figure 15: Critical current of YBCO [001]-tilt grain boundaries with varying misorientation and measured at 4.2 K [35]](image)

The magnetic dependency of the $j_c$ of a grain boundary is strongly affected by the misorientation of the junction. Low angle misorientations are limited by flux creep and can be seen to relatively insensitive to applied fields because they are strongly coupled. In addition, the magnetic field dependencies produce Fraunhofer-like patterns which become more distorted and pronounced as the misorientation angle is increased. As the magnetic field is increased the behaviour of the junctions becomes more hysteretic because flux pinning inside the grains causes the grain boundary vortices are pinned.
1.4.3 Applications of Josephson Junctions

There are numerous practical uses for Josephson junctions which include superconducting quantum interference devices (SQUIDs), superconducting quantum interference filters (SQIFs), superconducting vortex flow transistors (SVFTs) and rapid single flux quantum (RSFQ) electronics.

There are several different types of SQUIDs comprising of DC SQUIDs, RF SQUIDs and $\pi$-SQUIDs to name but a few. SQUIDs are highly sensitive magnetometers which are used to measure extremely small magnetic fields to about 5 aT with noise levels of 3 fT/Hz$^{1/2}$. The first type of SQUID produced was the DC SQUID, which relied on the DC Josephson effect, in 1964 by Jaklevic [36]. This consisted of two Josephson junctions in parallel, creating a loop. Without an applied magnetic field the supercurrent would be evenly distributed between both branches.

![Figure 16: A DC SQUID loop which has been biased and a field applied perpendicular to the surface](image)

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37
This means that the phase difference between the two branches can be shown to be

$$
\psi_a - \psi_b = \frac{2e}{h} \oint A \, dl = \frac{2\pi \Phi}{\Phi_0} \tag{1.20}
$$

assuming the contour goes through the interior of the superconductor and is well away from the edges. Using trigonometric identities and equation (1.23) the current is then simply given by

$$
I = I_c (\sin \psi_a + \sin \psi_b) = 2I_c \cos \frac{\pi \Phi}{\Phi_0} \sin \left( \Phi_b + \frac{\pi \Phi}{\Phi_0} \right) \tag{1.21}
$$

When considering the maximum supercurrent this equation reduces to

$$
I_{\text{max}} = 2I_c \left| \cos \frac{\pi \Phi}{\Phi_0} \right| \tag{1.22}
$$

Figure 17: $\Phi_0$-periodicity of a DC SQUID, each maximum represents an additional flux quantum entering the SQUID loop

It is important to note that at first it would appear advantageous to have the loop size as large as possible because this would give the largest flux change given a change in applied magnetic field. However, the modulation depth of the maximum supercurrent decreases with increasing loop inductance. Therefore, it is important to balance these two requirements. This
is where the inductance parameter comes in. This parameter is a ratio between the coupling energy stored in the junctions and the magnetic energy stored in the loop and is defined as

\[ \beta_L = \frac{2\pi LI_c}{\Phi_0} \]  

(1.23)

It is also important to consider the noise properties of the SQUID due to thermal fluctuations as well. This is the ratio between the thermal energy and the Josephson coupling energy and is given by

\[ \Gamma = \frac{2\pi k_B T}{I_c\Phi_0} \]  

(1.24)

The first high-\( T_c \) device was made by Koch \textit{et al} \cite{Koch1987} soon after the discovery of high-\( T_c \) materials in 1987. Early high-\( T_c \) DC SQUIDs generally consisted in the geometry of a square washer because this design was most prominently used in low-\( T_c \) designs. However, most devices with this geometry were considered inadequate for the majority of applications because of the relatively small effective area. However, by increasing the size of the washer the resolution of the devices was also increased to \( 150 \, \text{fT/Hz}^{1/2} \) for frequencies of 1 kHz, shown by Tanaka \textit{et al}. \cite{Tanaka1989}. Tanaka \textit{et al} also showed that comparable performance could also be achieved using flux focussing plates. However, the \( 1/f \) noise on these devices is generally quite high and bias reversal usually used to reduce this noise has been ineffective because of limitations brought about by vortices moving within the washer.

Subsequently, other designs emerged which minimised \( 1/f \) noise. One such device is the directly coupled magnetometer. This uses a large pickup coil directly connected to the SQUID structure and was used to induce a screening current with the SQUID. Koelle \textit{et al}. \cite{Koelle1991} investigated this setup and were able to create a SQUID with \( 1/f \) noise of \( 145 \, \text{fT/Hz}^{1/2} \) using a 20 pH SQUID coupled to a 47 mm\(^2\) pickup loop down to 1 Hz. Subsequently, this was improved by Lee \textit{et al}. \cite{Lee1992} by matching the inductances of the SQUID and the pickup loop more closely and achieved results of \( 35 \, \text{fT/Hz}^{1/2} \) and \( 65 \, \text{fT/Hz}^{1/2} \) at 10 kHz and 1 Hz respectively for a 50 pH SQUID using bias reversal.
Another method used to reduce 1/f noise in DC SQUIDs is to couple the device to a superconducting transformer [41]. The transformer consists of a pickup loop and a multi-turn input coil. By applying a field to the pick loop, a supercurrent is induced within the pickup coil, which conserves the total magnetic flux. This in turn induces a supercurrent within the multi-turn coil which is coupled to the SQUID. A major advantage of this setup is that the use of a multi-turn input coil allows the inductances of the SQUID and the pickup coil to be equally matched by simply changing the number of turns on the input coil, optimising the flux transfer into the SQUID. By considering Faraday’s law of induction this can be viewed mathematically by

\[
A_{\text{eff}} = \frac{A_p M_i}{(L_i + L_p) \pm A_s}
\]  

(1.25)

where \(A_{\text{eff}}\), \(A_s\), and \(A_p\) are the effective areas of the magnetometer, the bare SQUID and the pickup loop respectively, \(L_i\) and \(L_p\) are the inductances of the input coil and the pickup loop and \(M_i\) is defined by \(M_i = \alpha(LL)\). It was that \(\alpha\) strongly depends on the SQUID design and that the magnetic field gain is constant by coupling the transformer to different SQUIDs. Two methods have been used to create these types of system; flip chips magnetometers and integrated magnetometers.

Flip chip systems are formed in two parts, the SQUID and the flux transformer, which are then held together using a suitable adhesive. The first magnetometers using this fabrication method were reported by IBM (Oh et al. [42]) and Berkeley (Miklich et al. [43]). However, the lowest magnetic field noise was achieved by Dantskers et al [44] using an 81 mm² pickup loop and a 16 turn input coil coupled to a 500 μm washer SQUID with bicrystal junctions. This gave noise values of 8.5 fT/Hz\(^{1/2}\) and 27 fT/Hz\(^{1/2}\) at 1 kHz and 1 Hz respectively [41].

An alternative to flip chip magnetometers was found in the integrated magnetometer. This attempted to improve the inductive coupling between the SQUID and the input coil by integrating them on to the same chip, thus reducing the distance between them to the thickness of the substrate. These devices exhibited the best performance in terms of noise reduction with some groups reporting values of 9.7 fT/Hz\(^{1/2}\) and 53 fT/Hz\(^{1/2}\) for measurements at 1 kHz and 1 Hz respectively correspondingly by Drung et al. [45]. Despite these impressive measurements integrated magnetometers suffered from some problems. For
example, $V-\Phi$ curves suffered from distortions as a result of parasitic capacitance between the input coil and the SQUID washer. Additionally, the yield of these devices is much smaller than that of flip-chip multilayer devices.

Another approach to increasing the effective area is the multi-loop magnetometer. This essentially involves connecting a number of loops in parallel which not only increases the effective area of the SQUID but also reduces the inductance in the device. The first high-$T_c$ realisation consisted of an YBCO-STO-YBCO sample, with two 24° bicrystal junctions. This produced a magnetic field noise of 18 fT/Hz$^{1/2}$ and 37 fT/Hz$^{1/2}$ at 1 kHz and 1 Hz respectively, using a flux locked loop at 100 kHz flux modulation and bias reversal. This was produced by Ludwig et al [46]. Similar devices were also made by but used either step junctions, producing noise levels of 30 fT/Hz$^{1/2}$ [47] or different materials [48].

![Figure 18: rf SQUID with an LC resonant circuit consisting of an inductor and capacitor. The values are chosen to resonate at a specified rf frequency](image)

Single junction radio frequency (rf) SQUIDs are also another type of SQUID. These incorporate just one junction into a ring which is inductively coupled to an external driving circuit, shown in Figure 18. These driving frequencies range from a few hundred megahertz to a few gigahertz [1]. Given that the Josephson junction can support a phase difference of $\psi_a - \psi_b$ the SQUID quantisation is
The DC Josephson relation shows the supercurrent through the junction as

\[(\psi_2 - \psi_1) + 2\pi \frac{\Phi_T}{\Phi_0} = 2\pi n\] (1.26)

The supercurrent can also be determined in terms of the loop inductance and flux penetrating the loop as

\[I = I_c \sin \left(2\pi \frac{\Phi_T}{\Phi_0}\right)\] (1.27)

By considering the total flux \(\Phi\) through the loop we see that

\[\Phi = \Phi_{ext} + L\] (1.29)

where \(\Phi_{ext}\) is the applied flux, \(L\) is the inductance of the loop and \(J\) is the loop current. As \(J = I_c \sin \varphi\) where \(\varphi = -2\pi \Phi / \Phi_0\) we can reduce the total flux to

\[\Phi = \Phi_{ext} - LI_c \sin \left(2\pi \frac{\Phi}{\Phi_0}\right)\] (1.30)

This shows that given certain conditions, the response of the rf SQUID will either be linear or it will have a hysteresis depending on the difference in total flux.
Figure 19: Outputs of an rf SQUID. This shows the hysteretic behaviour that is associated with different amounts of flux in the system [16]

From this it is possible to see that the rf SQUID like the DC SQUID has a $\Phi_0$-periodicity. The rf SQUID has an advantage compared to that of the DC SQUID in that it does not require a transport current applied to it and therefore the operation of it is much more reliable.

However, at low temperatures (~4.2K) the DC SQUID is much less noisy than the rf SQUID. Nonetheless, the difference in noise levels at 77K between the rf and DC SQUIDs are negligible meaning that many measurements at this temperature can be performed by rf SQUIDs [7].

The first high-$T_c$ rf SQUID magnetometers was created by Zhang, et al. [49] and consisted of a large YBCO washers with a step edge junction on STO substrates. The SQUID was then inductively coupled to an LC tank circuit which resonated at 20 MHz. This was later increased to 150 MHz to increase the flux to voltage transfer coefficient. This SQUID could be operated in both hysteretic and non-hysteretic, both of which gave transfer functions of more than 40 $\mu$V/$\Phi_0$, a field sensitivity of 0.9 fT/Hz$^{1/2}$ [49] and noise of 170 fT/Hz$^{1/2}$ [41]. The noise value is of particular note since this is high compared to that of DC SQUIDs. Additionally, the inductance of this SQUID was estimated to be 240 pH, which is far larger than a DC SQUID. However, by coupling the rf SQUID to a flux concentrator the noise was reduced to 60 fT/Hz$^{1/2}$ down to 5 Hz.
1.5 Sample Fabrication Methods

There are a number of ways to fabricate thin film samples and numerous factors to consider which can influence the quality and properties of the thin films. These include the substrate compound, the method of deposition, the method of etching and the way in which electrical contacts are made on the sample.

1.5.1 Substrate Selection

The first factor to consider is the substrate structure. In order to create a stable thin film the lattice parameters of the substrate should be approximately equal to the lattice parameter of the thin film. In general, substrates used in the production of thin film superconductors are made using SrTiO$_3$ (STO) or MgO, with in-plane lattice parameters of 3.905 Å and 4.212 Å [50]. This is because the lattice parameters are approximately equal to that of a number of superconductors. For example, YBCO has lattice parameters of 3.81 Å and 3.88 Å for $a$ and $b$ respectively [51] which means that although the thin film would be under a small amount of tensile strain, it would not have a negative impact on the properties of the material. If, however, this did have a negative impact on the properties of the film then buffer layers could be used to match the lattice parameters of the substrate with those of the thin film.

It is also important to consider the thermal expansion coefficient of both the thin film and the substrate since these can also influence both the electrical and mechanical properties of the thin film. A large mismatch in the thermal expansion coefficients can, at worst, cause the failure of the thin film by cracking. For example, YBCO has a thermal expansion coefficient in the range of 9 x 10$^{-6}$ K$^{-1}$ [52]. Given that STO and MgO have 11.1 x 10$^{-6}$ K$^{-1}$ [53] and 8.0 x 10$^{-6}$ K$^{-1}$ [54], this means that both the substrate and thin film would expand and contract at approximately the same rate.

It should be noted that it is possible to make devices using crystals that are misorientated to create a grain boundary. However, a more in depth overview of these are given in chapters 3 and 4.

1.5.2 Thin Film Deposition

There are a number of ways to deposit thin films on to substrates. These are separated into two groups; physical vapour deposition systems, such as evaporation and pulsed laser
deposition (PLD); and chemical vapour deposition systems (CVD), such as plasma enhanced CVD.

![Diagram of a simple evaporation chamber. This is the simplest method of depositing thin films](image)

The easiest and most convenient method of deposition is evaporation. This method involves evaporating source material, under a vacuum of approximately $10^{-4}$ Pa, which then condenses on the substrate. The thickness of this is dependent on two factors; the distance between the source material and the mass of the source material, and by assuming that the material is distributed evenly over the area of a hemisphere and is mathematically stated by

$$d = \frac{m}{2\pi r^2 \rho}$$

where $d$ is the thickness of the film, $m$ is the mass to be evaporated, $\rho$ is the density of the substance to be evaporated and $r$ is the radius from the source to the target. To optimise this method and ensure the purity of the film it is necessary to ensure the purity of the source material and have a high rate of deposition, therefore minimising the amount of gaseous impurities included in the thin film.

There are a number of slight variations to evaporate the source material including thermal and electron beam methods as well as flash and resistive evaporation, with the method used depending on the source material and desired properties of the thin film. Thermal evaporation
involves placing shot, powder or wire into a ceramic boat. A large current is then passed through the boat causing the source material to exceed its vapour pressure.

The electron beam method involves a similar process whereby an electron beam, up to 15 keV, is used to heat the source material. The advantages of this method over thermal evaporation are that this process allows excellent control of the film thickness. Additionally, this method also offers high material utilization and control of the morphological and structural characteristics of the thin film. However, filament degradation can cause a non-uniform deposition rate and the electron beam can produce x-rays and stray electrons that can damage substrates.

Flash evaporation involves feeding a wire directly on to a hot ceramic bar which then evaporates on to the substrate. Resistive evaporation is accomplished by passing a high current directly through the source material, which is usually in the form of a foil or wire. However, this method limits the film thickness due to the size of the foil or wire. During evaporation deposition the deposition rate and film thickness can both be monitored and controlled using a quartz thickness monitor.

An advanced form of evaporation deposition is molecular beam epitaxy (MBE). It is a method of depositing a single crystal, under high or ultra-high vacuum (10^{-6} to 10^{-8} Pa). Each constituent of the film is contained, with ultra-high purity, in separate Knudsen effusion cells. These Knudsen cells consist of a crucible, heating filaments and a shutter and allow for accurate control of each layer. Upon evaporation the elements do not interact with each other or any vacuum chamber gases until they have condensed on the surface of the substrate, where they may chemically react with one another. The typical deposition rate of this process is less than 3000 nm per hour, allowing the film to grow epitaxially. This combined with the ultra-high vacuum means that the films produced are of the highest quality and purity.
Another PVD system is sputter deposition. This involves using a sputtering gas to eject source material from a solid target. It usually involves using a plasma, such as Ar\(^+\), which is confined near the surface of the target using magnetic fields. The ions follow the magnetic field lines in helical paths, which ionise more neutrals near the surface and increase the rate of deposition. The sputtered atoms are neutrally charged and freely pass through the magnetic trap and are deposited on the substrate.

There are a number of advantages of using this system over evaporation. Firstly, this method allows materials with high melting points to be deposited on the surface of the substrate, while evaporation would be difficult. Moreover, sputtered films typically have better adhesion than films deposited via evaporation.

Pulsed laser deposition (PLD) is another example of a PVD system where a high powered laser is used to ablate the surface of the target. This vaporised material forms a plasma plume which is then deposited on the surface of the substrate. The main advantage for this system over sputter deposition is that layer-by-layer growth is relatively straightforward and that it is conceptually very simple.

Another method of deposition is chemical vapour deposition (CVD). This involves exposing the substrate to volatile precursor chemicals in a gaseous form, which either react together or
decompose on the surface of the substrate to create the desired thin film. The temperature of the substrate is critical since this can influence the reactions that take place.

There are a number of variations of CVD including low pressure CVD, Aerosol assisted CVD and rapid thermal CVD. However, one of the most common is plasma enhanced CVD (PECVD). By ionising the source gases it allows for a greater reaction rate and also means that the substrate temperature can be lowered.

1.5.3 Methods of Structuring Thin Films

Once the deposition of the thin film has been completed it may be necessary to structure the thin film for use in devices. In terms of superconductors, this may include bridges, junctions and loops as well as other structures. The first step is to produce a pattern of the structure on to a photoresist. This is simply a polymer which can be used to mask off areas to protect underlying areas when etching. This can be done in a multiple ways including photolithography and e-beam lithography. Generally the first step in any lithographic process is to apply a layer of photoresist, by spinning it on to the surface. Spinning the resist on, at approximately 5000 rpm, ensures a uniform layer with thicknesses up to 2.5 μm. This can then be baked and patterned. Upon completion of this step the methods diverge slightly. When patterning using photolithography the photoresist is exposed through a specially prepared mask, to light with a wavelength determined by the structure of the photoresist. It is essential to ensure that the mask is perfectly flat on top of the photoresist so that the pattern is accurately reproduced. Developing this removes any undeveloped photoresist and it can then be etched.

Another way to pattern a resist is to use e-beam lithography. Electrons are used to pattern an electron-sensitive resist. This process can also create nanometre sized structures because it overcomes the diffraction limit of light. The primary advantage it has over any other process is that it can be performed without using a mask because the beam can be focussed to form and write each pixel into the resist.

From this point the sample can either be wet etched, using a solution that will react with the thin film, or dry etched, where an ionised gas or electrons are used to remove material. Wet etching is the simplest method for etching and involves immersing the sample in a solution that will react with the film. The time that the sample is immersed depends on the rate at
which the thin film is etched and can be varied using temperature and etchant solution dilution. It should be noted that this method is generally used only for large structures since it is particularly susceptible to undercutting, where large cavities are formed under the photoresist.

Dry etching is slightly more complex as it requires the manipulation of ionised gases. Examples of this type of processing are ion beam milling and reactive ion etching to name two. Ion beam milling uses ions, usually Ar⁺, to pattern structures that can be nanometres in length, with high fidelity. This is accomplished by passing a gas over a high potential, before accelerating the gas towards the sample, which is oppositely charged. The sputter yield, which is the ratio of the number of ejected atoms to the number of incident ions is dependent on the incident angle, the energy of the ion, the masses of the ions and atoms and the surface binding energy. The advantages that this process has over wet etching are that the relatively high momentum of the ions means that there is only negligible diffraction. Furthermore, this process provides an anisotropic etch, which greatly reduces the amount of undercutting of the photoresist.

Reactive ion etching (RIE) uses chemically reactive plasma to remove material on the sample. This method involves initiating a plasma, which is dependent on the etch process, within the chamber and confining it using magnetic fields. The plasma is then drawn towards the sample because they are oppositely charged and removes unwanted material by reacting chemically with the thin film. Material is also removed by sputtering. Due to the direction of the plasma, RIE is capable of producing anisotropic etch profiles. However, the sputter yield is very dependent on a number of parameters including gas pressure and flow as well as the RF power applied to the plasma.

1.5.4 Electric Contacts
Once any structuring has taken place it is required to make electrical contacts in order to perform any electric transport measurements. This can be accomplished using either a conductive paste or ultrasonic bonding. Conductive paste is the simplest way to create electrical contacts whereby the paste is mixed with a thinner and is applied to the surface of the thin film. It is then possible to manoeuvre a wire into place, which can then be attached to any external circuitry. Alternatively, the contacts can be created by ultrasonic bonding. This method involves applying high frequency vibrations to the sample and wire to create a solid
state weld. This has the advantage of being able to create contacts that are of the order of micrometres in length. In either case the contacts should be as small as possible to reduce contact resistance. After making four contacts it would be necessary to check the ohmicity of these using a standard IV measurement. This can then be compared to values determined by the geometry and resistivity of the sample.

Four point measurements should be taken whenever possible, with two wires carrying the current and the other two wires measuring the voltage. This separation of voltage and current eliminates the impedance contribution of the wires and contact resistance since the current leads create a voltage drop, not only across the impedance but also across themselves. By measuring across the sample directly, only the sample’s impedance is measured.
2. Electric Transport Measurements of Sr$_{1-x}$La$_x$CuO$_2$

Abstract

Electric transport measurements were taken of epitaxial grown Sr$_{1-x}$La$_x$CuO$_2$ (SLCO) thin films which were deposited on 36.8° symmetric and 45° asymmetric bicrystal grain boundaries (GB) to form Josephson junctions (JJ). RT measurements were taken under varying magnetic fields which were used to calculate the anisotropy of SLCO across a junction. It was found that the $T_c$ of each film was measured at 13 K and 16 K and had anisotropy parameters of $2.83 \pm 0.19$ and $2.25 \pm 0.03$ for the 36.8° symmetric and 45° asymmetric samples respectively. The main aim of the experiment was to determine the gap symmetry of SLCO because it has a simple structure and is related to more complex cuprates.

In order to do this, IV characteristics were taken at temperatures between 4.2 K and the $T_c$ of each sample and under magnetic fields ranging between 0 T and 11 T, across the film to measure the $j_c$ and across the junction to measure the coherence peaks and zero bias conductance peaks (ZBCP). The $j_c$, at 5 K, was measured at 13.4 kA·cm$^{-2}$ for the 36.8° symmetric bicrystal GB and 19.4 kA·cm$^{-2}$ for the 45° asymmetric bicrystal GB using a DC current method. Extremely large ZBCP were found which decreased with increasing temperature and magnetic flux density. This strongly suggests that SLCO superconductors are $d$-wave symmetric. However, the coherence peaks were not found and the integrated areas of the ZBCP were not conserved.

2.1 Introduction

After the discovery of high-$T_c$ superconductivity in LaBa$_2$Cu$_3$O$_{7-x}$ by Bendorz and Müller in 1987 [8], a great deal of research was performed on cuprates to create even higher $T_c$ superconductors, managing to raise the maximum $T_c$ from 30 K to 135 K. However, this led to the ever increasing complexity of structures of the compounds without understanding the underlying microscopic mechanism involved in causing the high-$T_c$ superconductivity. Logically speaking the Cooper Pairs (CPs) must form in the copper oxide (CuO$_2$) plane because this is the only common feature in all high-$T_c$ cuprates. Therefore, to understand the underlying mechanisms involved in high-$T_c$ superconductivity, such as the order parameter, it would be prudent to use a cuprate consisting only of CuO$_2$ planes.
2.1.1 Superconducting Surface States and Order Parameter Symmetry

Order parameters are simply functions that have a value of zero in one phase and a non-zero value in another and determine the behaviour of a material when it transitions from one phase to another. In the case of superconductors the order parameter has a zero value above $T_c$, $I_c$, and $B_c$ and a non-zero value below.

Currently, there is much debate about the mechanism involved in cuprate superconductivity, specifically whether it adheres to $s$-wave symmetry, $d$-wave symmetry or a mixture of the two. $S$-wave symmetry has an isotropic energy gap and U-shaped density of states. $D$-wave on the other hand is anisotropic, with nodes of alternating sign in the energy gap which signifies that the order parameter is angle dependant. It also has a V-shaped density of states. This difference is explained by considering the surface states of the respective symmetries.

![Figure 22: S-wave (left) and d-wave (right) order parameters. This shows the isotropic nature of the energy gap of s-wave order parameters and the anisotropic, nodal form of the $d_{x^2-y^2}$ energy gap](image)

In superconductors it is well known that quasiparticle surface states exist at the surface within the band gap of the bulk material similar to metals and semiconductors. Originally, de Gennes and Saint-James were able to describe these quasiparticle surface states for an insulator-normal metal-superconductor interface (INS) quantum well [55]. For an $s$-wave superconductor the energy of the surface states lie within the energy gap of the superconductor and depends on the surface properties. For a $d$-wave superconductor these levels may occur at the Fermi level because of the symmetry of the order parameter. It should also be remembered that when considering that the surface states at a junction, the
wavefunctions are seen to overlap and build up stationary states known as Andreev bound states, which represent the junction as a whole.

By considering a contact between a superconductor and a normal metal, and assuming that normal electrons in both electrodes have identical properties and can be assumed these electrons will have perfect transmission in the normal state. However, electrons which approach the interface from the normal metal to the superconductor with an energy inside the superconducting gap cannot penetrate into the superconductor or be classically scattered back. The solution to this is to have the electrons reflected as holes with the same momentum albeit with a phase shift of

$$-\gamma(E) \mp \chi$$  \hspace{1cm} (2.1)

where \( \chi \) represents the phase of the order parameter and

$$-\gamma(E) = \arccos\left(\frac{E}{|\Delta|}\right)$$  \hspace{1cm} (2.2)

represents the Andreev reflection phase shift, with \( \mp \) representing the fact that incident electrons are converted into holes and holes into electrons. This mechanism is known as Andreev reflection.

![Figure 23: Andreev reflection between a normal-superconductor contact. Incident normal electrons are reflected at the interface as holes with opposite spin, while two electrons in the form of a cooper pair, with opposite spins, are reflected back into the bulk](image)
It is easy to distinguish between $s$-wave and $d$-wave using the Bohr-Sommerfeld equation. Using quasiclassical arguments each quasiparticle trajectory represents a bound state with the energy given by the Bohr-Sommerfeld equation

$$-(\gamma + \bar{\gamma}) \mp (\chi - \bar{\chi}) + \beta(E) = 2n\pi$$

(2.3)

where $-(\gamma + \bar{\gamma}) \mp (\chi - \bar{\chi})$ represents the phase shift from the Andreev reflection and $\beta(E) = 2L(k^e - k^h) + \beta_0$ represents the contribution from propagation through the normal region. In the case of an $s$-wave with an isotropic order parameter this reduces to

$$-2\gamma + \beta(E) = 2n\pi$$

(2.4)

because for an isotropic, uniform order parameter $\gamma = \bar{\gamma}$ and $\chi = \bar{\chi}$. This also leads to the spectral equation

$$E = \pm \cos \frac{E \beta(E)}{\Delta}$$

(2.5)

This shows that the surface state always exists since $\beta_0 \neq 0$ even in a simple insulator-superconductor interface where $L = 0$. Furthermore, in an INS well this takes the form of

$$E = \pm \cos \frac{E}{\Delta} \frac{2L}{\xi_0 \cos \theta}$$

(2.6)

because the ballistic contribution $L$ becomes dominant and was found by de Gennes and Saint James [55]. At the Fermi surface there is no discernible difference between electrons and hole, and thus the density of surface states at the Fermi level is zero because there is no solution at $E = 0$.

In $d$-wave superconductors the order parameter is angle dependant, seen in Figure 22, and is given by

$$\Delta \theta = \Delta_0 \cos[2(\theta - \alpha)]$$

(2.7)

where $\alpha$ represents the orientation of the order parameter relative to the interface normal. In the case of a bicrystal interface, this is the angle of misorientation. If the order parameter has
the same sign before and after normal reflection, then the situation is not dissimilar to an anisotropic $s$-wave superconductor. On the other hand, if the signs of the incident and reflected order parameter are different then the Bohr-Sommerfeld equation is modified to

$-(\gamma + \bar{\gamma}) + \pi + \beta(E) = 2n\pi$ (2.8)

which always has a root at $E = 0$ with a surface state existing at zero energy. This is called a mid gap state (MGS) and is a direct cause of rotation of the order parameter. As a result, this is proof of $d$-wave superconductivity as this cannot exist within $s$-wave superconductivity. For an arbitrary value of $\alpha$, mid gap states exist within the interval of

$$\frac{\pi}{2} - \alpha < \theta < \frac{\pi}{2} + \alpha$$ (2.9)

Figure 24: (Left) Theoretical normalised conductance curve of $s$-wave/normal metal interface using the 2D-BTK model at $T = 0$ and $\gamma = 0$ with different values of the dimensionless barrier strength $Z = 0$, 0.2, 0.3, 0.5, 0.7, 1.0 and 2.0. (Right) $d$-wave superconductor/normal metal interface using the 2D-BTK model at $T = 0$ and the same values for $Z$ and $\pi/4$ as the angle between the direction of current and the $k_x$ axis [56].

This also led to the realisation that for $s$-wave superconductors, conductance is at a minimum at zero voltage. This this increases rapidly to a maximum at the superconducting gap, before
declining to the normal conductance of the material. D-wave superconductors on the other hand have an extremely large maximum at zero voltage which then quickly declines to the normal conductance of the material. The superconducting gap can sometimes be viewed as two shoulder features, however ability to view this depends on the film quality and barrier transparency. Examples of both s-wave and d-wave superconductors can be seen above in Figure 24.

2.1.2 The DC Josephson Effect and Mid Gap States
It is known that Andreev bound states are formed across junctions by the surface states of the superconductors and by extension a combination of electron and hole wavefunctions. The double quantum well is a clear model of this system and shows that the Andreev level will be shifted depending on both the transparency of the barrier and the phase difference across the junction. Furthermore, it can be seen that the Andreev levels will form Andreev bands via phase dispersion and have a width proportional to the transparency of the junction. These bands determine not only the critical Josephson current but also the Josephson current-phase relation.

The Andreev states are able to transfer current through the interface because charge is transferred during Andreev reflections. This current is also related to the phase dispersion of the Andreev state by

\[ I_x = \frac{2e}{\hbar} \frac{dE}{d\phi} \]  \hspace{1cm} (2.10)

and can be deduced from the thermodynamic equation

\[ I = \frac{2e}{\hbar} \frac{dF}{d\phi} \]  \hspace{1cm} (2.11)

This represents the microscopic free energy \( F \) of the junction [57]. Following this, the Josephson current of the bound states can be described as
\[ j_c = \frac{2e k_F}{\hbar} \sum_n \langle \frac{dE_n}{d\phi} n_F(E_n) \rangle \]  
\[ (2.12) \]

where
\[ \langle ... \rangle = \int_{-\pi}^{\pi} d\theta \cos \theta \]  
\[ (2.13) \]

### 2.1.3 Structure of Infinite Layer Superconductors

In order to investigate the mechanics of high-\( T_c \) superconductivity a basic compound consisting almost entirely of CuO\(_2\) planes needed to be created. One such compound was synthesised by Siegrist et al [58]. This consisted of CuO\(_2\) planes stacked in the c-axis direction separated by a divalent alkaline earth metal plane (A\(^{II}\)), such as strontium or barium, to form a compound with the form A\(^{II}\)CuO\(_2\). This is the parent structure for cuprate superconductors such as TBSCCO and is generalised by A\(^{III}\)A\(^{II}\)Ca\(_{n-1}\)Cu\(_n\)O\(_{2n+4}\)\(^+4\) where \( n \to \infty \). As \( n \to \infty \) it is also known as an infinite layer (IL) compound. The lattice structure of infinite layer compounds is that of a body centred cubic which form the equivalent of one huge crystal where all atoms are bound together by covalent or co-ionic bonds, rather than an aggregate of smaller crystalline structures bound together by electrostatic bonds because there isn’t a clear separation between molecules. Moreover, the features common to cuprate superconductors, such as apical oxygen and charge reservoir blocks, are not present [59].

This in turn means that A\(^{II}\)CuO\(_2\) crystals are not superconducting because there is a lack of free charge carriers. Therefore it is necessary to dope the IL crystals with an alkaline metal or by creating vacancies in the A\(^{II}\) plane it is possible to create a hole doped sample. It should be noted that currently the only hole based IL compounds that are superconductive are formed by creating vacancies and not by stoichiometric substitution and therefore may be substantially different to the parent structure. Alternatively, it is possible to dope with a member of the lanthanide series, such as lanthanum, to create an electron doped sample. This is one of only two electron doped superconductors, the other being T’ superconductors, such as La\(_2\)CuO\(_4\) [60], which are significantly more complex in their structure. Therefore, by systematically doping with different elements or changing the oxygen content in the charge reservoirs it is possible to control the charge carrier density in the CuO\(_2\) planes.
As previously stated, all superconductivity in cuprate superconductors takes place in the CuO$_2$ layer, specifically the $d_{x^2-y^2}$ orbital of the copper and the $p_x$ and $p_y$ orbitals of the oxygen which is shown in Figure 25.

![Figure 25: Electron orbitals of the CuO$_2$ plane. The Cu atoms are located in the centre exhibiting $d_{x^2-y^2}$ orbitals. The O atoms are located in the corners of the unit cell and exhibit $p_x$ and $p_y$ orbitals.](image)

Sr$_{1-x}$La$_x$CuO$_2$ (SLCO) is one such high transition temperature cuprate superconductor belonging to the infinite layer (IL) family of compounds, which is also an electron doped superconductor making it of particular interest. Additionally, it has a relatively high maximum $T_c \approx 43$ K when optimally doped [61], which makes it suitable for fundamental research.

![Figure 26: Structure of a Sr$_{1-x}$La$_x$CuO$_2$ unit cell. The CuO$_2$ planes are separated by atoms of Sr or La.](image)
2.1.4 Synthesis of Infinite Layer Superconductors

In spite of having a simple structure, IL compounds have been extremely difficult to synthesise because it requires high pressure to form a single crystalline structure. It is therefore simpler to create high quality single crystal thin films by using the epitaxial effect to mimic the high pressure needed. Originally, most IL samples were prepared on SrTiO$_3$ (STO) substrates which had a lattice constant $a_{\text{STO}} = 3.905$ Å [50]. However, the in-plane lattice constant of e-doped IL is $a_{\text{IL}} \approx 3.95$ Å. This difference in the in-plane lattice parameters of the substrate and the IL caused the Cu-O bonds to be compressively strained which resulted in a reduction in the superconducting properties of the IL [62]. A buffer layer consisting of Pr$_2$CuO$_4$, which had an in-plane lattice parameter $a_{\text{PCO}} = 3.962$ Å, was introduced in an effort to relieve this compressive strain to some success [63]. KTaO$_3$, with a lattice constant $a_{\text{KTO}} = 3.989$ Å, was also used as a substitute to STO which put the IL under tensile strain [64, 65]. This allowed the superconducting state of the IL thin film to emerge. However, the best results added a buffer layer of DyScO$_3$ which had a lattice parameter $a_{\text{DSO}} = 3.944$ Å [66]. This caused the IL thin film structure to be in a relaxed state because $a_{\text{IL}} \approx a_{\text{DSO}}$ and therefore increased the superconductive properties.

Typically these films are deposited using either PLD or MBE because these provide enough energy to form a homogenous film. However, after deposition excess O$^{2-}$ ions were found to form around interstitial sites in the A$^{\text{II}}_{1-x}$L$_x^{\text{III}}$ planes. This has the effect of suppressing superconductivity for two reasons. Firstly, the O$^{2-}$ ions have a large ionic radius which causes disorder in the crystal lattice, and in addition to this, it also causes the confinement of free charge carriers. Excess O$^{2-}$ ions can be removed using a vacuum annealing process. Nevertheless, care should be taken as reducing the overall oxygen content of the film too far can actually suppress superconductivity by producing oxygen vacancies in the CuO$_2$ plane. In some instances this can even create a new superstructure known as an infinite layer-related phase (ILRP).

2.2 Preceding Experiments

A number of phase sensitive experiments have been conducted to determine the symmetry of cuprate superconductors. These rely primarily on finding qualitative signature of unconventional superconductivity rather than the magnitude of the Josephson current. These
include SQUID interferometry, single Josephson junction modulation, tricrystal and tetracrystral magnetometry and thin film magnetometry.

Initial SQUID interferometry experiments, performed by Wollman et al., seen in Figure 27, composed of a single crystal of YBCO with weak links arranged at the edge or corner of the sample and relied on the quantum interference effects of the junction or SQUID.

![Figure 27: YBCO single crystal experiments used by Wollman et al. a) shows the corner SQUID configuration b) the edge SQUID configuration c) the corner junction and d) the edge junction [67]](image)

The corner SQUID configuration consisted of two orthogonally positioned (ac- and bc- respectively) YBCO-Pb weak links around a single crystal of YBCO. It was expected that if YBCO was indeed a d-wave superconductor then there would be a π-phase shift between the weak links. This was achieved by measuring the response of the SQUID’s critical current against externally applied magnetic field $\Phi_a$ since

$$I_s = I_a \sin \gamma_a + I_b \sin \gamma_b$$  \hspace{1cm} (2.12)

where $I_{a,b}$ and $\gamma_{a,b}$ are the critical current and phases of the junctions $a$ and $b$ respectively, if the phase is constrained to a single value i.e.

$$2\pi n = \gamma_a - \gamma_b + \varphi + 2\pi \left( \frac{I_a L_a}{\Phi_0} - \frac{I_b L_b}{\Phi_0} + \frac{\Phi_a}{\Phi_0} \right)$$  \hspace{1cm} (2.13)
where $L_{a, b}$ are the self inductances of the arms of the ring and $\varphi = 0$ or $\pi$, depending on whether the configuration of the ring is a ‘0-ring’ or ‘$\pi$-ring’. In ideal conditions, where the inductance parameter $\beta L < 1$, the $I_c$ has a maximum for a 0-ring and a minimum for a $\pi$-ring at $\Phi_a = 0$ respectively.

Plotting the phase shift as a function of DC magnitude and extrapolating for zero current an inference of the intrinsic phase shift of the device could be calculated. By doing the same with the edge SQUID, where both arms of the SQUID were located on the same side of the crystal it was possible to discern any differences in the phase shift. The result of these experiments showed that the 0-ring had an intercept of 0 while the $\pi$-ring had an intercept of between 0.3 and 0.6 $\Phi_a$ and is seen below [67].

![Figure 28](image-url)

**Figure 28:** The phase shift, as a function of DC magnitude, of the edge and corner SQUID. The corner SQUID exhibited a phase shift of ~0.5 $\Phi_a$ compared to the edge SQUID [67]

Nonetheless, this experiment had a number of complicating factors including twinning effects; because of the orthorhombic nature of the structure of YBCO it would mean that there might be a mixture of both positive and negative phases; flux trapping, demagnetisation and field-focusing effects due to system geometry, and the manner in which data was extrapolated. However, experiments by Brawner et al. [68] gave consistent results that indicate that these factors had very little, if any, effect of the results of the experiment.

Another experiment, performed by Schulz et al. [69] and based on the low-inductance SQUID with spatially distributed design of Chesca consisting entirely of YBCO 0- and $\pi$-
rings showed a nearly ideal result, with a minimum at zero applied field for the \( \pi \)-ring because the self inductances were negligible.

Single Josephson junction modulation has also been used to determine the symmetry of the order parameter. Wollman et al. [67] performed experiments on edge and corner junctions because these were less sensitive to flux trapping and sample geometry. If both geometries exhibit uniform current distribution and are considered ‘short junctions then it is expected that edge junctions will show the typical Fraunhofer pattern of critical current against flux penetrating the junction, with a maximum around 0 for both \( s \)-wave and \( d \)-wave symmetry. The corner junction, on the other hand, would produce a maximum at zero field for an \( s \)-wave superconductor while a minimum would be produced in the Fraunhofer pattern in the case of a \( d \)-wave superconductor.

![Fraunhofer patterns produced by edge junctions (left) and corner junctions (right) showing their respective maxima and minima](image)

Figure 29: Fraunhofer patterns produced by edge junctions (left) and corner junctions (right) showing their respective maxima and minima [67]

The findings of Wollman et al. did not entirely agree with the theoretical predictions but this was most likely due to asymmetries in the current densities and flux trapping within the junction. Qualitatively similar findings have also been reported by Hyun, Clem and Finnemore [70] as well as Vernik et al. [71].

Another way to investigate the order parameter symmetry was first proposed by Geshenkenbein and Larkin [72, 73] using frustrated geometry to spontaneously generate a half-integer flux quantum. This was realised experimentally using tricrystal and tetracrystal configurations. Creating a multi-junction loop on specifically orientated substrates allowed for the direction of the pair wave function. Depending on whether the devices exhibit a half-integer flux quantum or not allowed one to differentiate between to various order parameter symmetry.
Tsuei et al. [32] conducted an experiment where an epitaxial YBCO film, with thickness of 1200 Å, was deposited on an SrTiO$_3$ (STO) tricrystal substrate with orientation angles $\alpha_{12} = 30^\circ$, $\alpha_{31} = 60^\circ$ and $\beta = 60^\circ$, as shown in Figure 31 below.

Four loops, of inner diameter 48 μm and external diameter 58 μm, were then patterned using standard photolithographic and Ar$^+$ milling processes into the film: one across the tricrystal meeting point; two across bicrystal boundaries; and one ring with no junctions. Measurements showed that the self inductance was 100 pH and the $I_c$ was measured at ~1.8 mA. This meant that the product, $I_cL$, satisfied the condition necessary to observe a half-integer flux quantum, $I_cL >> \Phi_0$. 

Figure 30: Tricrystal Geometry showing the Miller indices of each segment and the respective angles between them

Figure 31: Experimental configuration of the $\pi$-ring tricrystal experiment of Tsuei et al. [32]
A scanning SQUID microscope image was taken of the tricrystal sample at 4.2 K in a field of less than 0.4 μT. The image shows $\Phi_0/2$ flux trapped within the centre ring while the other control rings have no flux trapped. These are only visible because of minor changes in inductance in the SQUID when passing over them.

Chesca et al. used tetracrystals to create YBCO based DC $\pi$-SQUIDs to observe $d$-wave induced zero-field resonances [30]. Observations of these DC $\pi$-SQUIDs showed that circulating AC currents, with frequency equal to the Josephson frequency, were induced by the $d_{x^2-y^2}$ symmetry of the order parameter.

Chesca et al. also used similarly designed La$_{2-x}$Ce$_x$CuO$_{4-y}$ spatially distributed junction (SDJ) SQUIDs on tetracrystals to investigate electron doped cuprate superconductors [29]. SDJ SQUIDs comprise of two junctions with widths that are non-negligible compared to the width of the hole of the SQUID. These junctions are considered to be in the small limit and are also characterised by a negligibly small inductance parameter $\beta_L$.

The samples themselves consisted of a SrTiO$_3$ tetracystal substrate which was specifically chosen to provide geometrically frustrated system such that in the case of a $d_{x^2-y^2}$ order parameter one junction would behave as a $\pi$-junction while the other would operate as a normal junction, creating a $\pi$-SQUID. In the case of an $s$-wave superconductor the device would operate as a conventional SQUID. A thin film of $c$-axis orientated La$_{2-x}$Ce$_x$CuO$_{4-y}$ with
a thickness of 0.5 μm was epitaxially grown. The film was then patterned using the standard methods used for photolithography and Ar⁺ milling.

The results showed very distinct differences in the magnetic field dependence for the π-SQUID and the 0-SQUID. The most obvious is that they indicate an intrinsically induced π phase shift because the 0-SQUID provided a maximum at zero field, while the π-SQUID produced a minimum with the offset of 60 pT caused by residual magnetic fields within the cryostat. The fact that these results are in very good agreement with theoretical data means that there is strong evidence for a predominant $d_{x^2-y^2}$ order parameter.

![Figure 33: Diagram of π-SQUID and 0-SQUID made by Chesca. The π-SQUID was made using a tetracryystal and had an intrinsic π-phase shift compared to the 0-SQUID [30]](image)

![Figure 34: 0-SQUID (left) and π-SQUID (right) showing integer and half integer flux quantisation respectively [29]](image)
Formation of surface states at zero energy has been observed previously in conductance measurements on a number of occasions in a number of experiments forming so-called zero bias conductance peaks (ZBCP). These experiments ranged from scanning tunnelling microscopy (STM) of YBCO by Kashiwaya et al. [74], in planar tunnel junctions by Covington et al. [75] and in grain boundary junctions by Alff et al. [76]. Additionally, ZBCP have also been observed in other cuprate superconductors such as Bi-2212 and Tl-2212. These are predicted in a number of studies such as those conducted by Yang and Hu, Bucholtz et al. [77] as well as Tanaka and Kashiwaya [78] who predicted that the density of Andreev bound states would be maximal on the [110]-orientated surface of a d-wave superconductor. Yang et al. [79] also predicted that there would be Andreev bound states on other surface orientations and grain boundary interfaces. This was supported by experimental data from Wei et al. [80] using [100], [110] and [001] orientations. All this theoretical and experimental data seems to imply a strong relationship between d-wave pairing and the occurrence of ZBCP.

Additionally, there have been numerous experiments involving Sr$_{1-x}$La$_x$CuO$_2$ (SLCO). These involve works on the temperature and magnetic field dependencies, its anisotropy and phase sensitive experiments to determine the pairing mechanisms involved in the superconducting state of SLCO. Changing the substrate, and thereby the lattice parameter, has also been experimented with in an attempt to improve the superconducting properties of the film.

The temperature dependency and ideal doping levels have been investigated numerous times. Er et al. [61] and Kikkawa et al. [62] found the optimally doped samples had a value of around $x = 0.10$ which gave a $T_c\text{ onset} = 43.5$ K and a $T_c\text{ zero} = 30.5$ K. Changing the doping levels between $x = 0.05$ and $x = 0.12$ found very little change in the onset of the phase transition, this being between 43.5 K for $x = 0.05$, 0.10 and 42.0 K for $x = 0.12$. However, the doping levels greatly affected the onset of the pure superconducting state, these being 18.0 K for $x = 0.05$, 30.5 K for $x = 0.10$ and 22.5 K for $x = 0.12$.

Tomaschko et al. [81-84] conducted a number of measurements on SLCO, with $x = 0.15$, on a 24° BaTiO$_3$-buffered SrTiO$_3$ bicrystal substrate. Junctions were fabricated using standard photolithographic and Ar$^+$ milling processes with measurements conducted at zero magnetic field. The critical temperature $T_c$ was found to have an onset at 19 K and reached zero at 15
K. The critical current density $j_c$ was ascertained to be 1.4 kA·cm$^{-2}$ at 4.2 K. This value corresponds to being two orders of magnitude smaller than YBCO GBJs but two orders of magnitude larger than T$^\prime$-compounds. Electric transport properties were also taken under magnetic fields ranging from 0 to 1.82 μT. The $j_c$ dependency on applied magnetic field of the junction was found to display a typical Fraunhofer pattern for a range between -30 μT and 30 μT. Fiske resonances were also found to appear at equidistance voltages of 316, 167 and 31 μV for 10, 20 and 100 μm junctions respectively. However, the most interesting and relevant part of this study was its work on quasiparticle tunnelling spectra. Curves were measured using a lock-in technique. By measuring the differential conductance, $dI/dV(V)$ and integrating between -15 and 15 mV, the density of states was found to be constant. The superconductor subgap was found to be v-shaped with some roundedness caused by thermal smearing and lifetime limiting processes. Moreover, the subgap becomes more pronounced with decreasing temperature. These findings are in line with the theory of a nodal order parameter ($d$-wave) rather than a fully gapped order parameter ($s$-wave). However, the conductance spectra of the junctions did not show a zero bias conductance peak (ZBCP), probably due to suppression of the ZBCP by strong disorder at the barrier. Suppression of the ZBCP is not unknown and had been found earlier with Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$, a $d$-wave superconductor.

Furthermore, Jovanovic et al. [85, 86] presented a study on a highly c-axis orientated SLCO thin film, with thickness of 450 Å and $x = 0.12$. The films were deposited on KTaO$_3$ single crystal substrates and were in-situ oxygen reduced under Ar whilst cooled. It was found that the critical temperature $T_c = 23$ K with relatively narrow transition compared to other cuprates of 4 K. The $T_c$ was also measured under increasingly large magnetic fields which showed a marked decrease in $T_c$ as the applied field increased. Moreover, the coherence length at zero temperature $\xi(0)$ of the $ab$ and $c$-planes was calculated using the values of the upper critical field $H_{c2}$ and the Ginzburg-Landau expression

$$ H_{c2} = \frac{\Phi_0}{2\pi\xi^2} $$

(2.14)

to obtain values of 46 Å and 3 Å for the $ab$ and $c$-planes respectively. The anisotropy $\gamma$ of the sample was found to be approximately 15 using the equation
The critical current density, $j_c$ at 4.2 K was found to be $14 \text{kA}\cdot\text{cm}^{-2}$. It was also found that while both $j_c(H_{\parallel})$ and $j_c(H_{\perp})$ decreased with increasing field, the effect on $j_c(H_{\parallel})$ was markedly weaker than $j_c(H_{\perp})$. The decrease in $j_c(H_{\parallel})$ was related to the low anisotropy of the compound and weak intrinsic pinning in the microstructure of SLCO. Moreover, the $j_c$ dependence on magnetic field orientation was not two-dimensionally angularly scaled such that the $j_c(\theta, H) \neq j_c(H_{\perp} = H\sin\theta)$. It was concluded that from these results that SLCO appeared to be much less anisotropic than BSCCO due to well coupled CuO$_2$ planes and represented more conventional behaviour.

In conclusion, there have been a number of phase sensitive experiments on both cuprate superconductors and their parent structure- infinite layer superconductors, with varying degrees of success. These involved various designs of SQUIDs and junctions using single crystals and bi-, tri- and tetra-crystal.

### 2.3 Sample Fabrication and Experimental Method

#### 2.3.1 Sample Fabrication and Preparation

The samples used in this experiment were made by Victor Leca at Universität Tübingen, Germany and consisted of a single, unpatterned SLCO grain boundary junction. The substrates comprised of two, 5 mm by 10 mm, [001]-tilt STO bicrystals with a misorientation of 36.8° and 45° respectively. A buffer layer of BaTiO$_3$ (BTO) was epitaxially deposited on top of this which had an in-plane lattice parameter $a_{\text{BTO}} \approx 3.994$ Å. This placed the SLCO layer under a small amount of tensile strain which improved its superconductive properties. A 34 nm layer of SLCO was deposited by pulsed laser deposition (PLD) with a further 10 nm Au layer deposited to decrease contact resistance.

The samples were fixed to the sample holder using low temperature varnish. Four point electric contacts were made in the corners of the samples using silver paste and gold wire. In order to prevent the silver paste from drying quickly 2-butoxyethyl acetate was used as the thinner as opposed to the standard thinner, which had a much higher rate of evaporation.
Figure 35: Electric contact setup on SLCO samples when measuring the ZBCPs. The GBJJ is shown as a dotted line. Silver paste contacts were placed in the corners of the sample (grey) while the gold layer (yellow) remained un-etched.

2.3.2 Experimental Method

Initially, measurements were taken with the Au layer completely intact to preserve the oxygen content within the sample. It was also thought that given the resistance of the junction, which was estimated at 0.1 Ω because Tomaschko et al. found a 50 μm junction was 10 Ω at 4.2 K. After fabrication and preparation of the samples, they were encased in a μ-metal shield and then inserted into the Sumitomo pulse tube cryocooler. This was pumped down to a pressure of ~10^{-4} mbar and a few mbar of helium gas was added to aid the transmission of the cooling power of the compressor to the sample head. Once the compressor had been started it took approximately 4 hours to cool the sample down to 4.7 K. During this cooling phase, the resistance dependence on temperature (RT) was measured using a Keithley 2400 Sourcemeter and a Keithley 2182A Nanovoltmeter to supply the current and record the voltage response respectively. An IV measurement was also taken above $T_c$ to check the contact ohmicity of the sample.
After reaching 4.7 K, current-voltage (IV) characteristics were taken, both of the film and across the grain boundary, using the same instruments as in the RT measurements. To conduct each measurement the temperature was set on the Lakeshore 340 Temperature Controller and allowed to settle such that there was less than a 0.01 K variation in temperature at the beginning of the experiment. Whilst measuring the IV characteristics of the film it was required to start the measurement at different current biases to reduce the amount of sample heating, which would reduce the overall $I_c$. Therefore, an initial IV curve was recorded from 0 mA to +40 mA to observe the general trend at 4.7 K. After recording this baseline value of $I_c$ at 4.7 K, each IV curve was ramped from ~2.5 mA below the $I_c$ to ~2.5 mA above the $I_c$. The downward sweep was disregarded because Joule heating, from resistive state, would have induced a lower $I_c$ value. The IV curves were then imported into Origin and the current value at which the voltage permanently deviates from zero voltage was recorded along with the corresponding temperature.

Current-voltage characteristics were taken across the grain boundary, firstly with respect to temperature for both $I_c$ and conductance and then with respect to applied magnetic field.
Additionally, pulsed measurements were carried out for the 45° sample. To begin, the cryostat was filled with the optimal amount of helium, thereby maximising its cooling power.

When measuring the $I_c$ dependence on temperature, the measurement was started close to $I_c$ so that sample heating would reduce the $I_c$. Moreover, only the first half of the measurement (i.e. ramping the current up) was used because as soon as the sample transferred into its resistive state it produced a heating effect on the sample. This heating caused some hysteresis on the down sweep especially at lower temperatures where a larger bias current was required to drive the sample into its normal state.

For the conductance measurements, full $IV$ sweeps were taken initially from -40 mA to +40 mA for the 45° sample and -30 mA to +30 mA for 36.8° sample at temperatures ranging from ~4.75 K to 13 K. The data files obtained were imported into Origin. By interpolating 5000 points within each $IV$ curve and differentiating this data, the conductance, $dI/dV$, could be found at different temperatures. By using a Fast Fourier Transform (FFT) filter with a 5% cut off noise in the derivative was reduced while retaining the major features of the curves.

In addition, pulsed measurements were conducted on the 45° sample using the Keithley 6221 Sourcemeter and the Keithley 2182A Nanovoltmeter. Pulsed measurements involved applying the different bias current values through the sample in 1 ms pulses with a 0.1 ms delay to allow the voltage to settle. There was also a 200 ms gap between pulses which allowed any Joule heating within the sample to dissipate thereby allowing more accurate $IV$ measurements. Additionally, the software provided with this measurement system allowed conductance measurements to be gathered from both current-voltage and from direct conductance measurements.
Furthermore, since applying a magnetic field is equivalent to raising the temperature of a superconductor, the dependence on the applied magnetic field was also investigated. A small electromagnet, with 114 turns and a radius of 15 mm, was attached directly behind the sample on the other side of the sample holder. This meant that the sample was situated 8 mm from the centre of the electromagnet. The electromagnet current, $I_{\text{mag}}$, was varied from -400 mA to 400 mA in steps of 50 mA which produced a maximum magnetic field strength of 2.2 mT. However, given the small magnetic field producible by such a coil it was necessary to use a superconducting magnet to produce higher fields.

Figure 37: The instrument setup on the liquid helium cryostat, showing the connections between each of the instruments

To this end, additional measurements were taken under high magnetic field in a Cryogenic Ltd 12 T liquid helium cryostat. The magnet was composed of two coils; the inner coil was made of NbSn wire on a stainless steel former with an outer coil of NbTi on an aluminium former. These produced a maximum field strength of 12 T. Additional $RT$ measurements were taken under high magnetic fields. Applying magnetic fields to superconductors is well
known to reduce the $T_c$ of all superconductors. However, the amount by which the $T_c$ is reduced is entirely material dependent. Measuring the $T_c$ dependency on applied magnetic field also allows for the calculation of the upper critical field, $H_{c2}$, as well as the coherence lengths $\xi_{ab}$ and $\xi_c$ for the $ab$- and $c$-planes respectively. From this the anisotropy, $\gamma$, was calculated. Further current-voltage measurements were taken to analyse the effect of applied magnetic field on the conductance peaks.

After this it was realised that the resistance of the Au layer, this being approximately 0.5 $\Omega$, may act as a shunt resistor in parallel with the SLCO layer. Subsequently, measurements were also taken with the Au layer removed across the boundary to remove any possibility of shunting from the Au layer. If there was any shunting through the Au layer then these measurements allowed the other conductance measurements to be normalised. The Au layer was etched using a solution of iodine (I$_2$), potassium iodide (KI) and water in the ratio of 4 g : 1 g : 10 ml. Large Ag paste contacts, roughly 8 mm$^2$, were used to create a basic, cross shaped mask. These contacts were left in place at first, however, after measuring the samples these were removed and replaced with smaller contacts.

![Figure 38: Experimental setup after the Au layer had been etched to have a gap of approximately 2 mm and re-bonded. This was used to measure the conductance across the GBJJ](image-url)
2.4 Experimental Results

2.4.1 36.8° Symmetric Bicrystal Grain Boundary Josephson Junction (GBJJ)

For SLCO deposited on the 36.8° bicrystal an initial resistance-temperature ($RT$) measurement was taken to determine the normal resistance just prior to transition, its critical temperature and to view any other notable features. As seen in the first set of measurements (Figure 39), with the Au layer completely intact, the normal resistance just before transition was 8.7 Ω giving a normal resistivity of 14.8 μΩ·cm. The transition occurred at 13 K over a period of 4.5 K upon which it showed a residual non-zero resistance of approximately 350 mΩ. This was caused by the normal resistance at the junction interface. Moreover, it can be seen that the transition has a foot structure in at around 12 K. The simplest explanation for this structure is that the film is not completely homogeneous and therefore multiple phases exist within the film that exhibit slightly different transition temperatures. An alternative explanation that Tomashko et al. suggested is that SLCO exhibits signs of thermally activated phase slippage (TAPS) in accordance with Ambegaoker and Halperins’ theory. Thermally activated slippage essentially describes the effects of thermal fluctuations on the phase of the order parameter across the Josephson junction. Near the transition temperature the coupling of the order parameters on either side of the junction can be disrupted because thermal energy, $k_BT$, becomes comparable to the Josephson coupling energy.
Additionally, further RT measurements were taken under high magnetic fields. Applying magnetic fields to superconductors is well known to reduce the $T_c$ of all superconductors. However, the amount by which the $T_c$ is reduced is entirely material dependent.

**Figure 39**: Resistivity-temperature dependence for the 36.8° bicrystal GBJJ SLCO sample across the junction

**Figure 40**: RT dependence across the 36.8° bicrystal GBJJ for different applied magnetic fields. (a) The perpendicular fields ranged from 0 T to 3 T. (b) The parallel fields ranged from 0 T to 11 T
The results of these experiments can be viewed in Figure 40. The \( RT \) measurements under a perpendicular field showed a steady decrease in \( T_c(0) \) and \( T_c(H_{c2}) \) with increasing magnetic field, with the highest measurable curve being taken at 3 T. Increasing the field further meant that the sample was in its mixed state at the system’s lowest possible temperature. On the other hand, the \( RT \) measurements for the parallel field could be collected for a full range of fields because the maximum field of 11 T was unable to reduce the \( T_c \) to the point where it was below the minimum system temperature. Additionally, the \( RT \) measurements from the parallel field showed somewhat unconventional and incongruous behaviour. Despite this, there was a general trend that could be seen in the reduction of \( T_c \) but it was very inconsistent.

Another noteworthy point is that the foot structure was preserved, in relation to its position within each measurement, for the perpendicular fields but seemed to be suppressed under certain fields when a magnetic field was applied parallel to the sample. This could simply be due to the magnet ramping incorrectly during certain runs, inhomogeneity within the film causing different phases to react differently to increasing fields, or simply an inaccuracy within the instruments.

Despite this, the upper critical fields for both parallel and perpendicular fields could be calculated using a linear extrapolation to zero temperature. A linear extrapolation was used because the behaviour displayed is vastly different to conventional superconductors with weak electron-phonon coupling, which is modelled by Werthamer-Helfand-Hohenburg (WHH) theory. This has also been noted by Jovanovic et al. [84, 85]. This gave upper critical fields, \( H_{c2}(0) \) of 53.85 ± 4.60 T and 6.72 ± 0.33 T for fields parallel and perpendicular to the \( ab \)-plane respectively, shown in Figure 41. Using equations 2.14 and 2.15 the coherence length was calculated at 70.0 ± 1.7 Å for \( \xi_{ab} \) and \( \xi_c \) to be 24.7 ± 1.0 Å. From these values the anisotropy parameter, \( \gamma \), was found to be 2.83 ± 0.19. This value is a lot less than that found by other groups, usually around 15. This would suggest that the CuO\(_2\) planes are not as well coupled as films used by other groups because the sample was not optimally doped and would therefore have inferior electric transport properties when a magnetic field was applied.
Figure 41: Upper Critical Field ($H_{c2}$) temperature dependence of the 36.8° bicrystal GBJJ across the junction for both parallel (black squares) and perpendicular field (red circles) showing the highly anisotropic behaviour of the sample. Inset: a table detailing the equation used to model the line of best fit, as well as the values of the intercept, slope and coefficient of determination for parallel and perpendicular fields respectively.

In an effort to observe whether the Au layer had a shunting effect on the sample, it was etched and measurements taken to observe whether any normalisation was required. However, prior to this it was prudent to take an $RT$ measurement to observe any changes in normal resistance of the film and across the grain boundary.
The film $RT$ measurements, seen in Figure 42, show a distinct rise in resistivity before transitioning to the superconducting state at 13 K. The fact that this temperature did not change implies that the oxygen content in the sample remained the same despite removing the protective Au layer. Moreover, there is a foot structure observed at around 10 K. This has been observed in other film measurements such as those conducted by Tomaschko et al. Another obvious feature is that the 10 μA biased measurement is qualitatively noisier than the 100 μA biased. The explanation is simply that the intrinsic noise of the system becomes comparable to the signal for the 10 μA biased measurement but would not be such an issue for the 100 μA biased measurement. This would also account for the slight change in resistivity of approximately 0.5 μΩ·cm and the larger foot structure. However, most importantly, the resistance after transition is a non-zero value meaning that in fact there was a resistance in the sample, possibly because the formation of the contacts meant that it could no longer be considered an “ideal four point measurement”.

Figure 42: Resistivity-temperature measurements of SLCO thin film for current biases of $10^{-5}$ mA (black) and $10^{-4}$ mA (red) when the Ag layer had been etched but large contacts were used. Inset: $IV$ measurement at 25 K.
Figure 43: Resistivity-temperature measurements of SLCO 36.8° bicrystal GBJJ for current biases of $10^{-5}$ mA (black) and $10^{-4}$ mA (red). This had the Au layer etched and large Ag contacts.

The $RT$ measurements of the junction (Figure 43) show similar behaviour to the original $RT$ measurements with the protective Au layer on because the transition temperature remained at 13 K, with a residual resistance from the junction after transitioning. However, there are a few distinct features that are different. This includes the transition appearing to be sharper and doesn’t have a foot structure. Moreover, the normal resistance is reduced by approximately 1 Ω which is unusual because the cross section of the film had been reduced which should have caused the resistance to rise. This could have been caused either by the contacts being closer and bigger or because there was some parallel connection involved from an unknown source. An increase in normal resistance is also seen just before transitioning to the superconducting state. The residual grain boundary resistance appears to be around 350 mΩ, which suggests that some of the Au layer was intact. Also, there is a noticeable difference in resistance between the normal phase when using a $10^{-5}$ mA current and a $10^{-4}$ mA current. This is probably due to a higher noise to signal ratio on the $10^{-5}$ mA current.
After viewing these results and the current-voltage characteristics it was decided that the large contacts should be removed and replaced with significantly smaller contacts. The reasoning for this is discussed later when considering the current-voltage characteristics.

![Resistivity vs Temperature](image)

**Figure 44:** Resistivity-temperature dependency of SLCO thin film with small contacts. The bias current used for this measurement was $10^{-4}$ mA and had a ‘true’ four point contact setup.

Again, two sets of $RT$ measurements were gathered for the final set of $RT$ results for the 36.8° sample, one across the film and one across the grain boundary, with both showing a transition around 13 K (see Figure 44). The film measurements showed similar characteristics to previous measurements with a gradual rise in normal resistance prior to transitioning. Nonetheless, the normal resistance was also seen to increase which was expected due to the decrease in cross sectional area. In addition to this, the foot structure reappeared during the transition.
Figure 45: Resistivity temperature dependency of SLCO across the 36.8° bicrystal GBJJ with small contacts. The bias current used for this measurement was $10^{-4}$ mA.

Grain boundary $RT$ measurements showed a slight increase in resistance before transition. The normal resistance before transition was 16.8 $\Omega$, giving a resistivity of 28.6 $\mu\Omega\cdot\text{cm}$, shown Figure 45. Again, this displays a foot structure but it appears earlier in the transition before settling at a residual resistance of 400 m$\Omega$. This value is approximately 50 m$\Omega$ larger than the one found in the original experiment, with an intact Au layer. This value should be the true resistance of the grain boundary because there would be no possibility of a parallel connection with the Au layer. It implies that although the normal resistance changed slightly, the values for $H_{c2}(0)$ should remain the same, and therefore the coherence lengths and the anisotropy factor should be unaffected.

Current-voltage ($IV$) characteristics were also taken of both the film and across the grain boundary. The film $IV$s taken were used to measure the critical current and the critical current density thereafter. On the other hand, the $IV$s collected across the grain boundary were used to measure the conductance peaks and superconducting gap.
Initial measurements of the film showed a critical current value of 43 mA at 4.8 K. As the temperature increased, the $I_c$ decreased significantly until becoming normal at 10 K (see Figure 46).

![Figure 46: Current-voltage characteristics of the thin film at temperatures ranging between 4.8 K, which showed the highest $I_c$ and 10 K which showed an ohmic response.](image)

From the $IV$ characteristics gathered previously, the critical current density, $j_c$, was calculated given the film thickness and width of 34 nm and 0.5 cm respectively. A voltage criteria of 3 μV was chosen to measure the $I_c$ so that deviation from the $I_c$, due to noise was not included in the measurement. The $j_c$ was therefore found to be 25.4 kA·cm$^{-2}$ at 4.8 K. This decayed quickly with increasing temperature before becoming normal at 10 K.
When the Au layer had been etched more IVs were taken of the film. Initially, when the large silver pads were left in place this resulted in the critical current having a slight slope, rather than being vertical, shown in Figure 48. This meant that a resistance had been introduced into the system, with the likely culprit being the contacts. As stated previously, these contacts were used to mask off areas when the Au layer was being etched and were left in place to reduce wear on the sample. However, their proximity to each other seems to have caused the voltage connections to pick up some of the current and vice versa, creating essentially a two point probe rather than the conventional four point probe.
Figure 48: Current-voltage characteristics at temperatures between 5 K (black) and 10 K (dark red) of the thin film once the film had been etched and the large Ag paste contacts left in place. This resulted in a sloped $I_c$ which showed the presence of an extra serial resistance.

Since there was an additional resistance included in the $IV$ measurements it was decided that the critical current density would not be calculated. Instead, the contacts were removed and replaced with smaller ones that would more closely model that of a four point probe. After doing so, the $IV$ characteristics were re-measured.
The results of the re-measured $IV$s show that the vertical $I_c$ was recovered with little to no hysteresis (see Figure 49). Moreover, for these measurements a larger current was used to investigate the resistive state of the sample which showed a surprising result. Rather than transitioning to a normal state, it was actually found that the sample went into a state of flux-flow resistivity because this part of the $IV$ was still non-linear before becoming normal.

This also allowed for the thin film critical current, $I_c$, and therefore the thin film critical current density $j_c$ to be accurately calculated. The results of these are shown below in Figure 50. These show the typical decay behaviour associated with the temperature dependence of the critical current density. Given that the critical current at 5 K was found to be 22.8 mA it meant the value of $j_c$ was 13.4 kA-cm$^{-2}$. This is obviously a lot smaller than the value for $j_c$ when the Au layer was intact because the Au layer probably acted as a resistor in parallel with the SLCO film. Moreover, the sample entered a normal state at 5K when 38 mA was applied.
Figure 50: Thin film critical current density between 5 K and 9 K. This showed a $j_c$ of 13.4 kA·cm$^2$ at 5 K, which decreased quickly and became unreadable above 9 K.

Measurements of the $I_c$ were also taken using the pulsed measurement method. It was hoped that by reducing the heating effect associated with DC measurements using high currents it would be entirely negated using this method.

When measured using the pulsed current method the results show that even when 100 mA is applied across the film it does not enter a true ohmic state, and instead seems to enter a state of flux flow resistivity. Moreover, at currents exceeding 50 mA some overheating was noted at higher temperatures, which can be seen in areas of negative resistance. This is shown in Figure 51.
Figure 51: Pulsed IV characteristics between 5 K (black) and 13 K (navy), showing the critical current of the thin film before entering a state of flux-flow resistivity

The results of the IV characteristics showed that the film had a $j_c$ of 18.8 kA·cm$^2$ at 5 K and decreased in an almost linear fashion before becoming unreadable above 9 K (see Figure 51). This increase in $j_c$ can be attributed to the reduction in Joule heating because the current was applied in 0.1 ms pulses which allowed the sample to be kept at a near constant temperature, rather than a current that is always on.
Figure 52: Critical current density of the sample once it had been etched. This showed a near linear decrease from 18.8 kA·cm\(^{-2}\) at 5 K before becoming unreadable above 9 K.

Measurements across the boundary were made in an effort to characterise the superconducting gap and any conductance peaks. It should also be noted that all conductance peaks and integrated areas of the ZBCP are normalised to the fully etched sample at 13 K, shown in Figure 53.

Figure 53: (a) Current-voltage characteristics and (b) conductance peaks of the 36.8° bicrystal GBJJ, ranging between 5 K and 13 K. The conductance peaks were normalised to 13 K on the etched sample.
Obviously these IVs do not show an $I_c$ but instead show a resistive state because of Andreev reflection at the bicrystal grain boundary. The amplitude of these IVs decrease as temperature increases until $T_c$ is reached and a normal resistive state is shown. When the differential conductance was measured and normalised to the fully etched sample it showed an extremely large zero bias conductance peak with shoulders either side, with 90% of the curve falling within ±10 mV. It can be seen that as the temperature increases from 5 K to 13.5 K the height of the peak decreases from 66 arb. units to 2 arb. units, with the shoulders becoming less broad and eventually merging to become a single peak.

Integrating these peaks within 90% of the peak conductance gave a voltage of ±10 mV, should have given the density of states for each temperature, which was expected to be a constant value. However, this shows an exponential decay-like behaviour with a quick reduction in the integrated area of the ZBCP from 5 K to 10 K, before settling at a relatively constant value between 10 K and 13 K. For an ideal junction, which displays a tunnelling-like electric transport channel, the integrated area of the ZBCP is equivalent to the density of states. However, the integrated area shown below in Figure 54 is not conserved when the temperature is changed. This suggests that there is an additional non-tunnelling-like channel, such as a resistive-like channel.
Moreover, IVs were also measured using a pulsed system in an attempt to reduce Joule heating within the sample since the current was applied in pulses of 0.1 ms with an interval of 10 ms between pulses. This also meant having a low contact ohmicity was especially important for these measurements. An additional positive was that it was also possible to measure the conductance directly as well as differentiating the IVs.

The pulsed IVs did not differ substantially from the DC IVs collected previously. The only qualitative difference between them seemed to be that it was possible to put more current through the sample and therefore attain higher voltages. This translated into the differential conductance measurements where again there was very little difference between these measurements and the DC measurements. It showed very similar values for the zero bias anomalies, ranging from 64 at 5 K to 2 at 13.5 K. However, the shoulders of the curve actually turn out to be a lot larger, with 90% of the curve falling within ±17 mV compared to 10 mV for the DC measurement. Furthermore, the shoulders also display a distinctive interference-like pattern.

Figure 54: Integrated areas of the ZBCP for SLCO 36.8° bicrystal GBJJ with the Au layer intact between 5 K and 13 K. These were normalised to the integrated areas of the ZBCP at 13 K when the sample was fully etched with a "true" four-point contact.
The conductance was also measured directly using the instruments (see Figure 55). Again this showed a peak value for the zero bias anomaly at 5 K to be 64 arb. units and the shoulder features starting at around 6 mV for the 5 K measurement. However, these peaks all appear a lot wider with 90% of the peak falling within ±90 mV, which is far beyond the expected value for the superconducting gap. The reason for this is that this voltage is so large because of the way in which the measurements are performed by measuring the voltage for each point and then applying the formula

$$G = \frac{I_2 - I_1}{V_2 - V_1} \tag{2.16}$$

This, along with the fact that only 200 points could be used because of time restraints, meant that a large amount of averaging took place which caused the peak width to increase. This would not be such a problem when considering the differential conductance since 2000 points were interpolated within the data.

![Figure 55: (a) Differential conductance and (b) direct conductance measurements for the 36.8° bicrystal GBJJ between 5 K and 13 K. All measurements showed suppression of the ZBCP as temperature was increased](image)

The magnetic dependence of both the current-voltage characteristics and conductance was also evaluated. Initially a small magnetic field of up to ±2.2 mT, produced by an electromagnet, was used. The results of this showed no impact on the IV characteristics or the conductance peaks.
Higher magnetic fields were then used, and were shown to have a much larger effect on the both the IVs and conductance peaks. Firstly, the dependence was assessed when the field was perpendicular to the $ab$-plane.

![Figure 56: Normalised differential conductance for the 36.8° bicrystal GBJJ with magnetic fields ranging from 0 T to 4.5 T, applied perpendicularly to the surface](image)

The measurements taken from 0 T to 5 T in 0.5 T intervals show the IVs and zero bias anomalies being heavily suppressed (see Figure 56). Initial application of a 0.5 T field showed an extremely large suppression of the conductance peak from 65 arb. units to 46 arb. units. Further application of stronger fields had decreasing effectiveness in suppressing the zero bias anomaly. It was found that magnetic fields of 4.5 T or more were able to fully suppress the zero bias anomaly, which is corroborated by the $H_{c2}$ value at this temperature of 4.45 T.

Integrating the differential conductance measurements showed a large initial decrease in the areas of the ZBCP before plateauing as the sample reached $T_c$ (see Figure 57). Again this is due to conduction through another non-tunnelling like channel.
Figure 57: Integration of the ZBCP for the 36.8° bicrystal GBJJ when a field was applied perpendicular to the \( ab \)-plane. This showed a sharp decrease in areas as the magnetic field was increased from 0 T to 4.5 T. These were normalised to the value of the fully etched sample at 13 K.

Measurements were also taken for fields parallel to the \( ab \)-plane with field strengths ranging from 0 T, in 1 T intervals, up to a maximum of 11 T, shown in Figure 58. Again, this initially showed a large suppression of the zero bias anomaly with decreasing effectiveness as the field is increased.
Figure 58: Normalised differential conductance for the 36.8° bicrystal GBJJ with magnetic fields ranging from 0 T to 11 T, applied parallel to the ab-plane of the sample. Again the ZBCP were normalised using the fully etched sample at 13 K

Moreover, the amount by which the zero bias anomaly was suppressed by the magnetic field was not nearly as much as when the field was perpendicularly applied. For example, the sample had a conductance of 65 at 0 T but 38 under 11 T, whereas the zero bias anomaly was fully suppressed by a field of 4.5 T when applied perpendicularly. This fits given that the value for $H_{c2}$ was predicted to be 35 T at 4.5 K. Furthermore, it was seen that for the measurements at 0 and 1 T the peaks seemed to be far narrower than expected.

Once again, the integrated area of the ZBCPs showed an exponential decline with increasing field meaning that there is an extra non-tunnelling-like channel through which transportation of quasiparticles can take place (see Figure 59). The initial value at zero field is also the same as the perpendicular field which is to be expected, given that there is no trapped flux or residual fields at the time of measuring. However, the gradient of the parallel field is a lot lower than the perpendicular field because of the highly anisotropic behaviour of the sample.
The angle dependence of the sample showed highly anisotropic behaviour. The experiment was conducted under a field strength of 3 T and rotated from a parallel position to perpendicular in 10° intervals. In the parallel position the zero bias peak measured 52 arb. units - this value decayed to a value of 9 arb. units in a non-linear fashion, shown in Figure 60.
Figure 60: Normalised conductance measurements for the 36.8° bicrystal GBJJ at a temperature of 4.5 K and a magnetic field of 3 T. Measurements are shown for various angles $\theta$ of the magnetic field orientation and are relative to the thin film planar structure, between 0° and 90°.

The integrated area of the ZBCP for the angle dependence (see Figure 61) shows an exponential decay, from approximately 27 arb. units when parallel to 4 arb. units when the field is aligned perpendicular to the sample. This is due to the anisotropy of the sample as discussed previously.
By etching the sample across the grain boundary, it was hoped that any adjustment of the normalisation factor for the conductance peaks could be made if necessary. Initially the large silver contacts, which were used to provide a mask, were left in place as previously stated. By performing both DC and pulsed measurements on the sample, it was hoped that an accurate measurement of normalisation factor could be obtained.

The DC measurements showed a reduction of approximately a third in the value of the zero bias anomaly from 65 arb. units to 47 arb. units. This was to be expected given that there was no longer a parallel shunt resistance, in the form of the Au layer, bridging the junction. Moreover, it can be seen that there has been approximately a twofold increase in the peak width with 90% of the peak falling within ±21 mV. The shoulders of the peak are also more prominent and are twice as wide as previous measurements. Both these features suggested that there was a serial resistance within the system with the most likely source being the large contacts. Their size and distance to each other meant that they could no longer be considered a “true” 4 point contact since the current noise was able to interfere with the voltage measurement.
The integrated area for this setup shows unusual behaviour, whereby it follows an almost linear decrease in the integrated areas of the ZBCP to the $T_c$ of the thin film, which is in stark contrast to the exponential decay in the integrated areas of the ZBCP for the sample when the Au layer was fully intact. It would seem that in addition to the non-tunnelling-like behaviour observed in previous measurements there was an extra serial resistance. This can be implied from the IV characteristics of both the film and across the junction shown previously. This compounded the original non-tunnelling-like behaviour to produce a near-linear decline in the integrated areas of the ZBCP.
Figure 63: Integrated areas of the ZBCP for the 36.8° bicrystal GBJJ between 5 K and 13 K with DC measurements conducted on the etched sample with large Ag contacts.

The pulsed measurements of the etched sample with large contacts showed a small amount of broadening of both the shoulders and the peaks compared to the etched sample with DC and had slightly more noise within the measurement. This is probably due to the decrease in heating of the sample which would allow more features to become visible.

Figure 64: Pulsed $IV$ and conductance measurements for the 36.8° bicrystal GBJJ once the sample had been fully etched between 5 K and 13 K. The conduction measurements were normalised to 13 K.
Integration of the ZBCPs showed that the area was suppressed greatly as the temperature was increased. Initially, this was linear between 5 K and 7.5 K before tailing off to the value at normal resistance. Again, this further supports the idea that there was an additional non-tunnelling channel through which conduction took place.

By removing the large contacts and reapplying smaller ones, it was hoped that the effect of the widening of the conductance peaks and shoulders of the curve, seen in the previous set of experiments, would be negated.
Figure 66: (a) Temperature dependence of the current-voltage characteristics and (b) normalised conductance peaks for the 36.8° bicrystal GBJJ once it had been fully etched sample and measured with a "true" four-point contact

The results of these experiments show another decrease in conductance to 40 arb. units at 5 K because of an increase in resistance associated with the contacts being further apart. However, both the peak and shoulder width returned to approximately the values recorded of when the Au layer was fully intact (10 mV), with 90% of the peaks falling within 13mV. This signified that the serial resistance, likely introduced by the large contacts, had been removed.
Again, pulsed measurements were taken to remove any effect of heating on the sample. Due to the removal of the heating effect it allowed more current to be applied to the sample. In this case 100 mA was used which can be seen in the IVs, and enabled the resistive state to be viewed. The ZBCP can be viewed in the centre of the IVs around zero voltage, which can then be seen to enter a non-linear resistive state before entering ohmic behaviour.

Figure 67: Temperature dependence of the integrated areas of the ZBCP for the 36.8° bicrystal GBJJ, once the sample had been fully etched sample and normalised at 13 K.

Figure 68: The pulsed differential conductance and measured conductance for the 36.8° bicrystal GBJJ once it had been fully etched and measured with a "true" four point contact.
Both the measured and differential conductance peaks show a slight decrease in the maximum value of the ZBCP compared to the values from the un-etched sample and the etched sample with large contacts. Once more, this is due to a reduction in the cross sectional area across the boundary, compared to the un-etched sample. However, both these measurements seem to be wider than the pulsed measurements with the Au layer intact, with 90% of the peak falling within 33 mV for the differential measurement and 220 mV for the directly measured conductance. Some small structures were found on the shoulders of the differential measurement in the range of -10 mV to 10 mV. The fact that these structures also appear in the results of the un-etched sample suggests that these are features of the zero bias anomalies and not artefacts created by the instruments.

Figure 69: (a) The integrated area of the ZBCP for the 36.8° bicrystal GBJJ from the differential conductance and (b) the measured conductance. Again these were integrated to include 90% of the ZBCP, which was ±33 mV and ±210 mV for the differential and measured conductances respectively.

2.4.2 45° Asymmetric Bicrystal Grain Boundary Josephson Junction (GBJJ)

Measurements of the 45° SLCO sample were much the same as those conducted on the 36.8° sample. These included RT measurements with the Au layer intact with different bias currents and in different magnetic field to gauge the anisotropy factor across the grain boundary. Further RT measurements were conducted once the sample had been etched to provide a ‘true’ four point contact across the sample, which aided in the normalisation of the data. It should be noted, however, that no measurements were conducted with large contacts since these were found to be inferior when measuring the 36.8° sample. Furthermore, current-voltage measurements were taken both across the film and across the grain boundary, to quantify the critical current and conductance peaks respectively.
Initially, *RT* measurements of the SLCO thin film were made both across the grain boundary and across the film. The first *RT* measurements were taken using bias currents of 100 μA, 10 μA and 1 μA. These showed the transition occurring over a 5 K gap, with the onset occurring at 16 K and entering the full superconducting state at 11 K. During transition the sample exhibited the same foot structure that had been seen both in the 36.8° sample and by other groups. This was thought to have been a consequence of different phases within the film having slightly different transition temperatures. The sample was also found to have a normal resistivity of 23.4 μΩ cm just prior to transitioning.

Additionally, there was an anomaly at around 7 K, which resulted in the resistivity briefly increasing before decreasing again. This anomaly seemed to be linked to the magnitude of the bias current used, whereby increasing the bias current resulted in a marked increase in the resistivity. This anomaly was probably the result of small cracks or fissures forming within the Ag paste contacts during the first couple of cooling runs. Another noteworthy observation is that the *RT* measurement using a bias current of 100 μA showed a vastly different normal resistance before transition to the measurements using 10 μA and 1 μA because of the increase in heating power, in this case 100 times more, than when using 10 μA. However, this measurement also had a larger signal to noise ratio than the other two measurements.

![Figure 70: Resistivity-temperature measurements of the 45° asymmetrical bicrystal GBJJ. (a) used bias currents of 100 μA (black), 10 μA (red) and 1 μA (green). Initially, these showed the same foot structure as the 37 sample as well as an anomalous increase in resistance at 7 K. (b) The anomaly seen at 7K disappeared after a few measurements](image)
A further *RT* measurement, shown in Figure 70 (b), using a bias current of 100 μA showed a slight decrease in normal resistance while the anomaly seen previously at 7 K had disappeared completely. This suggested that the structure of the contacts had settled, thereby reducing the overall contact resistance. Moreover, the foot structure, as seen in previous measurements, was still visible, with the onset of the transition occurring at 16 K over a 5 K range. The sample then became fully superconducting at 11 K. This is consistent with previous measurements of the sample.

*RT* measurements were also taken under different magnetic fields, ranging from 0 T and 6 T for fields applied perpendicular to the *ab*-plane and 0 T and 11 T for fields applied parallel to the *ab*-plane. As seen in Figure 71, both sets of measurements show a very linear decrease in the onset of transition, and are therefore in good agreement with the theory.

![Figure 71: Resistance-temperature dependence when (a) perpendicular fields between 1 T and 6 T and (b) parallel fields between 1 T and 11 T are applied to the *ab*-plane of the 45° asymmetrical bicrystal GBJJ](image)

The data, shown in Figure 71, was then used to calculate the $H_{c2}(0)$ value for both parallel and perpendicularly applied fields. The $T_{c,\text{onset}}$ was plotted against the applied field and extrapolated to zero temperature resulting in the intercept being the $H_{c2}(0)$ value of the parallel and perpendicular fields. These were shown to be $39.46 \pm 0.52$ T and $7.82 \pm 0.09$ T for parallel and perpendicular fields respectively. From this the coherence length $\xi_{ab}$ and $\xi_c$ were calculated at $64.9 \pm 0.4$ Å and $28.9 \pm 0.2$ Å respectively. These values compared favourably with those found for the 36.8° sample of $70.0 \pm 1.7$ Å for $\xi_{ab}$ and $\xi_c$ to be $24.7 \pm 1.0$ Å. This allowed for the anisotropy factor $\gamma$ to be calculated at $2.25 \pm 0.03$, which is significantly lower than those of the film values, of approximately 15, from other groups but
slightly lower than the value from the 36.8° symmetric sample of 2.83 ± 0.19. This implies that the CuO$_2$ planes in the 36.8° sample are coupled slightly better than the planes in the 45° sample.

Once these measurements had been completed it was decided, much like the 36.8° symmetrical bicrystal GBJJ, to etch the sample using a solution of I$_2$ and KI to assess the effect of keeping the Au layer intact. These included a number of $RT$ measurements of the film and across the junction to characterise any effect of the Au layer.

The first measurement was across the junction and showed the onset of transition to be 15 K and reaching a fully superconducting state at 11 K, which is in good agreement with previous results. Likewise, the foot structure has also been preserved and was in some respect more defined with respect to previous measurements. However, there was an increase in resistivity compared to previous measurements when the Au layer was intact, increasing from 23.4 μΩ·cm when the Au layer was intact to 49.5 μΩ·cm when the Au layer had been removed. This was to be expected given the decrease in cross sectional area, with the Au layer also

![Figure 72: Upper critical field dependency on temperature of the 45° asymmetrical bicrystal GBJJ. The upper critical field, $H_c(0)$, for parallel and perpendicular fields was recorded at 39.46 ± 0.52 T and 7.8 ± 0.09 T respectively.](image)
acting as a shunt resistance in parallel with the normal resistance of the junction. Additionally, the normal resistivity is seen to increase prior to transitioning, behaving more like a ceramic than a metal. The junction resistance was found to be 0.1 μΩ·cm

![Figure 73: Resistivity-temperature dependence of the 45° asymmetrical bicrystal GBJJ, using 100 μA (black) and 10 μA (red), once the sample had been etched to create a 'true' four point contact. This shows an increase in resistivity compared with the original measurements, while also displaying a more defined foot structure.](image)

The resistivity behaviour of the film was qualitatively similar to that of the junction in that prior to transitioning there was a moderate increase in resistivity before dramatically spiking. This jump was nearly 40% more than the background resistivity and occurred over a range of 3 K. Furthermore, the sample also exhibited a foot structure at exactly the same temperature as the junction measurement, suggesting this is an intrinsic feature of the SLCO, rather than the junction itself. However, this feature was proportionally a lot larger than that exhibited by the junction RT measurement. In addition to this, decreasing the current bias shows not only an increase in the noise to signal ratio which is to be expected, but also a decrease in normal state resistivity, the spike in resistivity and the foot structure and an increase in residual resistivity in the superconducting state.
Current-voltage characteristics were also taken across the film in an effort to measure the critical current density of the film. The $I_c$ at 5 K was found to be 33 mA and eventually disappeared at 12 K. Using the thickness of the film the $j_c$ was found to be 19.8 kA·cm$^{-2}$. This is consistent with the 36.8° sample which had a $j_c$ of 25.4 kA·cm$^{-2}$ at 5 K.
Figure 75: (a) DC current-voltage characteristic and (b) critical current density of the SLCO thin film with the Au layer intact. Measurements were taken from 5.3 K to 12 K.

Once again these measurements were repeated once the Au layer had been etched to check whether these had any effect on the attribute. It was found that at 5 K the $I_c$ was 33 mA, which gave a critical current density $j_c$ of 19.4 kA·cm$^{-2}$. This compares favourably with the value found from the 36.8° sample. However, this is also lower than the un-etched sample which adds further weight to the thought that the Au layer acted simply to perform as a shunt resistance.

Figure 76: (a) DC current-voltage characteristics of the thin film between 5 K and 16 K and (b) critical current density between 5 K and 12 K measured once the sample had been etched

Current-voltage characteristics were also taken across the grain boundary to assess the effect on the conductance peaks of different temperatures and magnetic fields. These are shown in the figure below. The first conductance peaks were collected with the Au layer intact with varying temperature. These results showed that as the temperature increased from 5 K, the
size of the peak decreased from 250 arb. units. Moreover, shoulder-like structures could be seen at 5 K occurring at ±0.25 mV. As the temperature increased these structures moved closer together and decreased in magnitude eventually forming one peak. Also, the coherence peaks of the superconducting gap were not observed at any voltage.

The ZBCPs at each temperature were then integrated between ±0.6 mV. Unfortunately, the current source was unable to produce enough current to generate a high enough voltage across the junction at 5 K and therefore this value was discarded. Nevertheless, the integrated areas decrease as the temperature increases, shown in Figure 78. This was unexpected because normally this would be constant and would be equal to the density of states across the junction. However, the fact that this happens implies that there is a non-tunnelling-like channel through which current flowed as well as the superconducting channel.
Figure 78: Temperature dependency of the integrated areas of the ZBCP for the 45° asymmetrical bicrystal GBJJ. This shows an almost linear decline in the integrated areas as temperature increases.

When the pulsed method was used to view the ZBCPs (see Figure 79), they were found to have heights of 288 arb units and 290 arb units for the differential conductance and directly measured conductance at 5 K correspondingly. These were slightly higher than the values found when using the DC method and so it is thought that using the pulsed method reduced sample heating, which in turn amplified the ZBCPs. Furthermore, the shoulder structures occur at a voltage of approximately 0.5 mV. This is almost double those collected using the DC method.
Figure 79: (a) Differential conductance and (b) measured conductance (bottom left) on the sample with the Au layer intact using the pulsed current method on the 45° asymmetrical bicrystal GBJJ. This was conducted at temperatures between 5 K and 10 K. Conductance measurements have been normalised to the conductance measured at 14 K once the sample had been etched and arbitrarily shifted to apart.

The integrated areas of the differential ZBCP showed similar behaviour to previous results, in that there was a non-linear decrease in the area which tailed off as the temperature tended towards $T_c$. However, all the values found in the pulsed differential result were roughly half those found in any other measurement of the 45° asymmetrical bicrystal GBJJ. This could be due to the fact that only 200 points were gathered for each ZBCP, which when processed caused an aberration within the data, resulting in an almost vertical differential conductance peak. In contrast, the measured ZBCP showed both nominal behaviour and values at each temperature. The fact that both of these show declining values in the integrated area puts forth more that there is at least one additional channel which is non-tunnelling-like within this sample.
Parallel magnetic fields were then applied to the sample to assess the effect of these fields on the ZBCPs and integrated areas. The conductance measurements show that at 1 T there are distinct shoulders to the peak while also having a main central peak. As the field is increased the shoulders are the first features to be suppressed. However, the central peak retains most of its magnitude declining from 208 arb. at 1 T units to 151 arb units at 11 T because the magnetic flux is not able to penetrate the sample fully.
Integrating the areas, between ±1.6 mV, of the ZBCP showed that the area was not conserved. The relationship between the integrated areas and the applied field appears to be highly disjointed with the areas decreasing at a large rate to begin with, between fields of 1 T and 5 T, before settling to a much lower rate between 5 T and 11 T. Normally it is expected that the area, and therefore the density of states, would be conserved since changing the applied field is analogous to changing the temperature of the sample. This suggests that once again that there is an additional conduction channel which is non-tunnel like through which current can flow.
When perpendicular fields were applied to the sample it showed that perpendicular field were highly suppressive of the ZBCPs. An initial measurement at 0 T shows a peak value of 238 arb. units which also has some secondary shoulders at ±0.20 mV and ±0.55 mV. When 1 T was applied the central peak and shoulders were suppressed significantly. The entire ZBCP was then fully suppressed when a field of 6 T was applied. This is in very good agreement with the value predicted by the $RT$ anisotropy experiments performed earlier on the sample which predicted a value of 5.6 T would be needed to suppress superconductivity at 4.5 K.
Figure 83: Normalised differential conductance peaks for the 45° asymmetrical bicrystal GBJJ when perpendicular fields ranging from 0 T and 5 T. Again this data was normalised to values gained from DC measurements at 14 K once the sample had been etched.

By integrating between ±0.75 mV to include 90% of the peak it was shown that the value of the integrated areas decreased dramatically at an exponential rate before settling. This decrease is again because the states are not conserved and instead flow through a non-tunnelling channel. These values are also a lot less than the parallel field values found and can be explained by the highly anisotropic behaviour of the sample across the grain boundary.
Figure 84: Normalised integrated areas of the ZBCP for the 45° GBJJ with varying magnetic fields applied perpendicular to the \textit{ab}-plane. These were normalised to data from the DC measurements at 14 K.

The sample orientation with respect to the applied field was also considered and the results are shown in Figure 85. Angles were varied between the parallel and perpendicular angles to the \textit{ab}-plane, in a field of 3 T. It showed that as the angle moves from parallel to perpendicular the peak height decays exponentially but is never fully suppressed. Initially, shoulders are present on the parallel measurement but these are gone by the next measurement at 10°. Moreover, the values found for the parallel and perpendicular fields are identical to those found at 3 T in previous experiments.
Figure 85: Current-voltage characteristics and differential conductance peaks of the 45° asymmetrical bicrystal GBJJ for different orientations, ranging from 0° to 90°, in a 3 T field. The conductance peaks were normalised to DC data gathered at 14 K.

Integration of the ZBCP areas (see Figure 86) showed that the parallel orientation had an area of 208 arb. units, which quickly descended to an almost constant value around 40 arb. units. This shows that at low angles the density of states are not conserved, however as the angle increases the integrated areas, and therefore the density of states, seems to remain relatively constant at angles exceeding 30°. This displays the highly anisotropic nature of the sample between the $ab$-plane and the $ac$-plane.
After the magnetic field experiments had been completed the sample was etched and current-voltage characteristics were taken again to assess any effect on the ZBCPs and also allow normalisation of the rest of the data collected.

The results of this showed that the first measurement at 5 K had shoulder structures at $\pm 0.4$ mV which were four times larger than the central peak at 600 arb units and 150 arb. units respectively. These shoulder structures decrease in magnitude and the voltage at which they occur also decreases as the temperature is increased. Upon reaching a temperature of 10 K the shoulder structures join the central peak and immediately produce a reflection-like event that disappears as the sample approaches $T_c$. 

![Figure 86: Angle dependence of the integrated areas of the ZBCP of the 45° asymmetrical bicrystal GBJJ in a 3 T field. DC data from the sample at 14 K was used to normalise the values, once it had been etched.](image-url)
Figure 87: Conductance peaks gathered for the 45° asymmetrical bicrystal GBJJ once it had been etched. Temperatures ranged from 5 K (black) to 14 K (purple). This data was used to normalise the preceding DC data. The conductance peaks were normalised to 14 K, with each peak arbitrarily shifted ~300 arb. units up to make it easier to view the peaks.

The integrated areas of the etched sample showed similar values to those found on the sample when it was not etched. For example, the integrated areas at 6 K are 93.2 arb. units and 100.2 arb. units and 2.49 and 3.30 at 13 K for the etched and un-etched sample respectively. The decrease in integrated areas also occurs at similar rates suggesting that the Au layer has very little effect on the overall results of the experiment. It also implies that the non-tunnelling-like channel is present within the SLCO itself. This is shown in Figure 88.
The pulsed current method was also used on the etched sample again to check whether the Au layer had any effect on the overall results and allowed the normalisation of previous pulsed method results. Moreover, we were able to apply more current across the junction, up to 100 mA, because this method used different instruments to the DC method. The resultant IV characteristics, seen in Figure 89, show that measurements between 5 K and 8K produce very little voltage, approximately 2 mV, despite applying a current of 100 mA. The voltage then rapidly increased with increasing temperature, regardless of the fact that the current amplitude was decreased.

After differentiating the IV characteristics, they showed that the ZBCPs had qualitatively similar behaviour to that displayed by the sample when it was measured using the DC method. For instance, the shoulder structures start at a significantly larger differential conductance than the central peak; these then gradually reduce in magnitude and the voltage difference between them decreases as the temperature increases. However, there are a number of quantitative differences between the differential conductances using DC and pulsed methods. For example, when considering the 5 K measurement the shoulder structures have a
magnitude of 542 arb. units on the DC method compared to the background conductance of the sample, whereas the shoulder structures have a magnitude 377 arb. units for the pulsed method. Moreover, the shoulder structures occur at ±0.75 mV when using the pulsed method compared to ±0.40 mV for the DC method. This discrepancy could be explained through sample heating which could cause the shoulders to broaden. Nonetheless, the central peaks measured 148 arb. units and 135 arb. units for the DC and pulsed methods respectively, when viewed at 5K. Therefore, this seems relatively unaffected by any heating produced using the DC method.

Figure 89: (a) Differential conductances and (b) measured conductances of the 45° asymmetrical bicrystal GBJJ once it had been etched between 5 K and 14 K. Conductance measurements were normalised to 14 K
The integral of each of the pulsed method ZBCPs was taken for both the differentiated and directly measured conductances. The integrated areas of the differentiated ZBCPs showed a small decrease from 128 arb. units to 91 arb. units over a range of 5K before steeply declining during transition to the normal state.

Integration of the directly measured ZBCPs showed similar behaviour and values at each temperature, where there was a small decrease in areas of the ZBCPs prior to transitioning. Upon reaching the transition temperature this value again decreased dramatically within just a few degrees.

![Graph](image)

**Figure 90:** (a) Integrated areas of the differential and (b) measured ZBCPs of the $45^\circ$ asymmetrical bicrystal GBJJ, which have been normalised to 14 K

### 2.5 Conclusions

In conclusion, $RT$ measurements were conducted on both the $36.8^\circ$ symmetric and $45^\circ$ asymmetrical bicrystal GBJJs. These showed that the $T_{c\text{ onset}}$ for the $36.8^\circ$ sample to be 13 K, with the transition occurring over a range of 4.5 K, which indicates that the sample was underdoped because an optimally doped sample has a $T_c$ of 43 K. This remained constant for both the measurements across the film and across the junction regardless of whether the Au layer was etched or intact. However, the normal resistance was affected by the Au layer. For instance, when the Au layer was intact the sample had a resistivity across the junction of 14.8 $\mu\Omega\cdot\text{cm}$ whereas it was recorded at 28.6 $\mu\Omega\cdot\text{cm}$ once the Au layer had been removed. Moreover, the residual resistance of the grain boundary was found to be 350 m$\Omega$ and 400 m$\Omega$ when the Au layer was intact and removed respectively. This means that the Au layer simply acted as a parallel resistance, shunting some of the current through the Au layer rather than
through the junction. Additionally, it was noticed that there was a step feature visible during the transition. The most likely cause of this is that the sample was inhomogeneous. This resulted in the sample having a number of separate phases within the SLCO film structure that had different transition temperatures and normal resistances. Once one phase had started transitioning a second phase, with a lower normal resistance, could be seen before transitioning at a lower temperature. An alternative explanation is that according to Ambegaoker and Halperin’s theory when the thermal energy, $k_B T$, approaches that of the Josephson coupling energy it causes the coupling of the order parameter across the junction. This is less likely because the step feature was noticed both across the film and the junction.

Similarly, $RT$ measurements of the 45° asymmetric sample showed it had a $T_c$ onset of 16 K and transitioning over a range of 5 K which indicates that the sample was under doped because this is much lower than the optimally doped $T_c$ of 43 K. This remained fairly constant when measured across the film or across the junction regardless of the Au layer being intact or etched. However, the normal resistance was affected by the removal of the Au layer because the resistivity increased from 23.4 $\mu\Omega \cdot \text{cm}$ to 49.5 $\mu\Omega \cdot \text{cm}$ once the Au layer had been etched. The step feature seen in the 36.8° symmetric sample appeared in these measurements as well as at around 13 K and was considered to be a consequence of having an inhomogeneous film as explained previously.

The coherence lengths and anisotropy factor were also found from $RT$ measurements conducted within a magnetic field. These showed that the upper critical field at zero temperature, $H_{c2}$, was found to be 53.85 ± 4.60 T and 6.72 ± 0.33 T for fields parallel and perpendicular to the $ab$-plane respectively for the 36.8° symmetric sample. These gave values for the coherence lengths of 70.0 ± 1.7 Å for $\xi_{ab}$ and 24.7 ± 1.0 Å for $\xi_c$. Thus, the value for the anisotropy parameter, $\gamma$, was found to be 2.83 ± 0.19.

The coherence length for the 45° asymmetric sample showed similar behaviour to the 36.8° sample. Firstly, the values for $H_{c2}$ were calculated to be 39.46 ± 0.52 T and 7.82 ± 0.09 T for parallel and perpendicular fields respectively. From this the coherence length $\xi_{ab}$ and $\xi_c$ were calculated at 64.9 ± 0.4 Å and 28.9 ± 0.2 Å correspondingly. This allowed the anisotropy factor $\gamma$ to be calculated at 2.25 ± 0.03. Obviously, both of these values for $\gamma$ are a lot smaller than the value found by Jovanovic et al. [85, 86] and can also be interpreted as a direct consequence of the samples being under doped.
Current-voltage characteristics were also taken both across the film, to find the value of the critical current density $j_c$, and across the junction, to find the conductance characteristics and any ZBCP. Firstly, $IV$ characteristics of the 36.8° sample across the film showed that the $j_c$ at 5 K was 25.4 kA·cm$^{-2}$. When the sample was etched this was reduced to 13.4 kA·cm$^{-2}$ which was likely due to the Au layer acting in parallel with the SLCO thin film, which would allow any excess current to be shunted through the Au layer instead of through the SLCO. Furthermore, it was noticed that the sample does not transition directly into a normal state. Instead it goes into a non-linear state of flux-flow resistivity, where flux lines penetrate and randomly move within the sample causing chaotic behaviour in the $IV$ characteristics. Upon reaching 38 mA at 5 K, the sample went into a normal state.

The pulsed current method was also used in an effort to negate any Joule heating created by applying a DC current across the sample. This reduction in Joule heating allowed the sample’s $j_c$ to be increased from 13.4 kA·cm$^{-2}$ to 18.8 kA·cm$^{-2}$. However, this improvement also meant that the resistive state of the sample was unable to be viewed and instead remained in a state of flux-flow resistivity.

DC values of the 45° asymmetric sample displayed similar $j_c$ values, at 5 K, of 19.8 kA·cm$^{-2}$ when the Au layer was not etched and 19.4 kA·cm$^{-2}$ when the sample had been etched. These values are in accordance with the values found for the 36.8° sample. However, both of these values are much smaller than the maximum value found in literature of 2 MA·cm$^{-2}$, though this is probably due to the sample being not optimally doped and being under an incorrect amount of strain, which would cause the electric transport properties to be inferior.

In addition to this, the ZBCPs temperature dependence was found using DC and pulsed current methods. Firstly, the ZBCPs temperature dependence of the 36.8° symmetric sample was highly dependent on temperature. Initial measurements at 5 K showed a peak of 66 arb. units which decreased until $T_c$ was reached. When the sample was etched and connected correctly, it reduced the peak to a value of 40 arb units which is probably due to the removal of the shunt resistance across the junction. The 45° asymmetric sample also displayed extremely large ZBCPs with the DC measurement at 5 K showing a peak height of 250 arb. units. DC measurements of the sample once etched showed that the peak height had shrunk to 150 arb. units, which was expected as the removal of the Au layer no longer allowed the
current to be shunted across the junction. It should be noted that this sample also demonstrated some peculiar behaviour where the shoulder structures, at ±0.4 mV, were four times larger than the central peak, at 600 arb units at 5 K. This could be due to the high misorientation across the grain boundary.

The peak height was larger for the 45° asymmetric sample than the 36.8° symmetric sample because the increased misorientation angle would increase the number of incident Andreev reflection events. This also explains the reason that both sets of these conductance measurements are far larger than those found in literature, because other groups had used grain boundaries with a lower misorientation.

Pulsed measurements on both samples substantiated the findings from the DC ZBCPs since there was very little difference between these measurements and the DC measurements. For example, it showed very similar values for the ZBCPs, ranging from 64 arb. units at 5 K, to 2 arb. units at 13.5 K. However, the shoulders of the curve actually turn out to be a lot larger than the DC measurement. Moreover, the shoulders also display a distinctive interference-like pattern. Additionally, the conductance was measured directly using the pulsed method. Again this showed a peak value for the ZBCP at 5 K to be 64 arb. units and the shoulder features starting at around ±6 mV for the 5 K measurement. However, these peaks all appear a lot wider with 90% of the peak falling within ±90 mV because of the non-linear dependence current has on voltage. The pulsed current method was performed once the sample had been etched as well. It demonstrated a reduction in the ZBCP peaks and was determined to be 43 arb units and 41 arb. units for the differential ZBCP and the directly measured ZBCP respectively. The outcome of the pulsed current method on the 45° asymmetric sample displayed reductions in the ZBCP height like the 36.8° symmetric sample. The ZBCPs were found to have heights of 288 arb units and 290 arb units for the differential conductance and directly measured conductance correspondingly at 5 K. Upon etching the sample, the values for the differential and measured conductances were recorded at 182 arb. units and 351 arb. units.

Importantly, shoulder structures were also present in all measurements at differing voltages and shrank with increasing voltage indicating that they are part of the ZBCP rather than signifying the coherence peaks of the superconducting gap. Unfortunately, the coherence
peaks, which would show the superconducting gap, were not visible in any measurements but this is not uncommon.

Integration of the ZBCP results showed that the areas were not conserved when the temperature was changed. Since in an ideal junction the integrated area of the conductance represents the density of states across the junction, it would be expected to remain constant. From this we can conclude that neither sample demonstrates ideal, tunnelling-like behaviour and that there is an accompanying non-tunnelling-like channel through which electric transport also takes place.

Magnetic fields were also applied at a number of angles and magnetic flux densities to evaluate their effect on the ZBCP using the DC method. When parallel fields were applied, at a temperature of 4.5 K, to the $ab$-plane it showed that the ZBCP of both samples were only marginally reduced in height by 18 and 58 arb. units for the 36.8° symmetric and 45° asymmetric sample respectively with fields ranging from 1 T to 11 T. The reason that these peaks were resistant to magnetic fields is because magnetic flux was unable to penetrate the c-plane SLCO film. From the anisotropy measurements it would be necessary to apply a field of 34.9 T for the 36.8° symmetric sample and 28.2 T for the 45° asymmetric sample. Integration of these ZBCPs revealed a decrease in the areas further substantiating the view that there is an additional non-tunnelling-like channel for electric transport.

Perpendicular fields on the other hand showed that they were easily able to suppress ZBCPs with fields above 6 T, at 4.5 K, on both samples because magnetic flux was easily able to penetrate the sample through the $ab$-plane, which corresponds with the values predicted by the anisotropy measurements 4.8 T and 5.6 T for the 36.8° symmetric and 45° asymmetric samples. Again this demonstrates the highly anisotropic properties of the SLCO. The integrated areas of the perpendicular field ZBCPs were also greatly reduced compared to that of the parallel field, indicating not only are the samples more susceptible to magnetic fields applied perpendicular to the $ab$-plane than those applied parallel, but also that there is an additional channel that is non-tunnelling-like, such as a normal conduction channel.

The angle dependence of both samples was also evaluated by rotating them within a 3 T field at 4.5 K between 0° (parallel to the $ab$-plane) and 90° (perpendicular to the $ab$-plane). The height of the ZBCPs for both samples decreased quickly at first between 0° and 20° but the
rate at which the peak decreased then slowed as it approached 90° because the relationship between the angle and flux penetration is dependent on \( \sin \theta \). This relationship was mirrored in the findings for the integrated areas of the ZBCP and was expected because the amount of flux penetrating the sample would increase proportionally to \( \sin \theta \).

Finally, the observation of a ZBCP strongly suggests that SLCO superconductors are \( d \)-wave superconductors. This supports measurements made by others on YBCO systems by Chesca et al. [29, 30] and Wollman et al.[66]. This also contradicts many previous reports which concluded that SLCO superconductors are \( s \)-wave superconductors.
3. Arrays of YBa$_2$Cu$_3$O$_{7-\delta}$ Josephson Junctions

Abstract

Arrays of Josephson junctions (JJs) have been used in multiple types of superconducting devices including superconducting quantum interference filters (SQIFs), Josephson vortex flow transistors (JVFTs) and microwave (MW) generators. Parallel arrays of bicrystal GBJJs were designed and fabricated using standard photolithography practices and ion beam milling. The arrays were characterised by a logarithmic distribution in loop areas and an inhomogeneous inductance over the entirety of the device.

Upon testing the device it was found that the $V_{dc}(I_{ctrl})$ output had a periodicity of 1.8 mA or 12 μT at temperatures above 77 K. The device performed extremely well as a Josephson vortex flow transistor (JVFT). It was found that the device was able to produce a gain of 19.2866 at 77 K when results for $I_{dc}(I_{ctrl})$ were analysed. Moreover, a switching behaviour was viewed at a number of temperatures where the device transitioned from a state of collective disorder, with the individual junction $I_c$s distributed randomly between $\pm I_c(max)$ to a very ordered state, where the vast majority of the junctions have a value of either $I_c(max)$ or $-I_c(max)$.

3.1 Introduction

There are multiple devices that rely on arrays of Josephson junctions. The most prominent are superconducting quantum interference filters (SQIFs) and vortex flow transistors (VFTs). Superconducting quantum interference filters (SQIF) were designed just over a decade ago by a team from Tübingen, Germany as a promising alternative to SQUIDs [87]. SQIFs are very similar to SQUIDs as they are simply an array of Josephson junctions connected in either serial, parallel or a mixture of both and are usually constructed on a bicrystal.

However, unlike SQUIDs the grating structure has to be irregular [88] (i.e. the loop sizes of Josephson junctions have to be non-commensurable) so that there is no common factor between the areas of the loops [87, 89, 90]. This means the voltage output $V_{dc}(\Phi)$ produced is a delta-like trough at zero magnetic field with a vanishing modulation everywhere else, though there maybe some symmetry about $\Phi = 0$. Consequently, it can be seen that the more chaotic and non-linear the loop sizes are the less likely the device will have any periodicity. In contrast, a single loop or a number of same size loops connected together create voltage
responses that are \( \Phi_0 \)-periodic. This property caused SQIFs to become a highly attractive prospect as magnetometers which are able to measure absolute magnetic fields since SQIFs are the only devices not hampered by a \( \Phi_0 \)-periodicity. This is shown in Figure 91.

![Figure 91: Outputs from a single SQUID, multi-SQUID loops and SQIF][90]

The profile of \( V_{dc}(\Phi) \) along with the width of the peak \( \Delta B \), the voltage span \( \Delta V \) and modulation outside of the peak \( \delta V \) can be modified simply by altering the loop distributions of size and order and the electrical properties of the Josephson junctions themselves. Ideally, \( \Delta V \) should be extremely large while \( \Delta B \) and \( \delta V \) should be kept to an absolute minimum [86, 88].
SQIFs have been developed in order to fulfil several different roles. For instance, they can be used to measure minute magnetic fields due to their lack of $\Phi_0$-periodicity [87-92]. They have also been used as broadband amplifiers and to mix signals [93-95].

The SQIF can detect a magnetic field when $I > I_c$, superposing the output from each loop together. In turn this cancels out all values of $V$ except when the magnetic field is zero, which constructively interferes. This turns the output signals from all the junctions into the archetypal $V_{dc}(\Phi)$ function as previously mentioned. The size of this delta-like trough is determined by the sensitivity of the SQIF to magnetic fields which in turn is dependent on the voltage to magnetic field transfer factor $V_B$ which is defined as

$$V_B = \max \left( \frac{\partial V_{dc}}{\partial B} \right) \quad (3.1)$$

Magnetic field measurements are made in two ways. One method, known as ‘zero field cooling’, simply cools the device below $T_c$ while shielding it from any magnetic fields. Once the sample is cooled below $T_c$, the shield is removed and the introduction of an ambient magnetic field causes the trough to shift from zero to the values of the Earth’s local magnetic field [91].
It is also possible perform the measurement by cooling the device in the presence of a magnetic field, known as field cooling. When the shield is introduced to the system, the trough shifts back to its zero position.

Results of magnetic field measurements have been promising with a number of experiments showing large transfer factors. For example, Oppenlander et al. [92] found values for $\Delta V = 3.5$ mV and $\Delta B = 1$ μT and a maximum magnetic field to voltage transfer factor of $V_B = 6000$ V/T when measuring a 112 loop SQIF which was coupled to an on chip pickup loop. This was fabricated using standard grain boundary junction technology.

SQIF have also been used as microwave amplifiers. Shadrin et al. [96, 97] constructed a SQIF device consisting of 20 loops in a serial array. This was constructed on NdGaO$_3$ (NGO) bicrystal substrates and used standard YBCO thin film technology. Operating within the regime where the Fraunhofer dependence of the $I_c$ and the flux focussing of the bicrystal junction geometry had been taken into account, it was found that the SQIF had a gain of $g = 20$ dB. However, the flux-to-voltage conversion factor was found to be $40$ mV/Φ$_0$ and the $V(\Phi)$ response was recorded as $12$ mV. Both these values were smaller than expected.

Figure 93: Output produced by a 112 loop SQIF by Oppenlander et al. This had a value of $\Delta B = 1$ μT, $\Delta V = 3.5$ mV and a transfer factor of $6000$ V/T [92]
Another class of devices that use arrays of Josephson junction are vortex flow transistors (VFTs). These are three terminal devices (TTDs) and the basic principles can be viewed using Landauer’s fluid controlled pipe, shown in the figure below. It shows that a large flow of fluid can be controlled using a relatively small control flow.

This principle can also be applied to other systems, which use faster moving entities such as electrons, fluxons or photons and was first proposed by Likharev et al. [98]. In superconductors the flow of electrons can be regulated using electric, magnetic fields or quasiparticle injection. TTDs which are controlled by electric or magnetic fields can be considered analogous of each other, with one being considered a transconductance device and
the other is considered a transresistance device while those controlled using quasiparticle injection cannot be considered to be a true TTD, since the quasiparticles are directly injected into the source-drain channel thereby mixing with the controlled flow [99].

Magnetic field effect TTDs can be split into two further categories by whether the vortices flow within the junction or within the film of the sample. If the vortex motion is controlled within the Josephson junction or array of junctions then the device is known as a Josephson vortex flow transistor (JVFT) [100-105]. If the vortex motion is controlled within a thin film then the device is known as an Abrikosov vortex flow transistor (AFVT) [106-108]. The sensitivity of AVFTs and JFVTs has been greatly debated with a consensus being reached that the JFVTs are likely to be the most sensitive because the sensitivity of the device depends on how sensitive the $I_c$ in the source-drain channel, is to changes in magnetic field. Given that the typical change needed in magnetic field needed to affect the $I_c$ of a high-$T_c$ weak link is approximately 100 μT, while the field needed for a thin film is in the region of 1 T [99]. This can be reduced by fabricating films with virtually no flux pinning, however this is technologically difficult.

The speed of JVFTs and AFVTs are also very different. Josephson vortices lack a normal core and there is minimal damping from quasiparticle currents across the junction. Also the velocity of the vortices is determined by the velocity of the electromagnetic waves in the transmission line of the array. This is typically $10^7$ ms$^{-1}$. In contrast Abrikosov vortices contain a normal core which causes strong damping of motion of the vortex itself. This means that the velocity of these vortices is much slower, usually between $10^3$ and $10^4$ ms$^{-1}$. Given that the upper frequency limit of JVFTs and AVFTs is the ratio of the maximum vortex velocity to their respective screening lengths, these being the Josephson penetration depth $\lambda_J$ and London penetration depth $\lambda_L$. The Josephson penetration depth is around 10 to 100 times larger than the London penetration depth. Therefore, the JVFTs have an upper frequency limit several orders of magnitude larger than the AFVTs [99].

Furthermore, the impedance of JFVTs and AFVTs are also very different. The impedance of a JFVT is determined by the normal resistance of the junction, which is usually several ohms. In contrast, the resistance of the flux motion in AFVTs is far smaller than the normal resistance due to the large upper critical field of high-$T_c$ materials. This is shown by
Thus, it is difficult to produce AFVTs with impedances of a few ohms.

Several groups have experimented with JVFTs. For example Gross et al. [99] fabricated a JVFT based on an YBCO thin film and grain boundary junction technology. From this they produced a JVFT consisting of 10 junctions which was asymmetrically biased and as inductively coupled to an on-chip control line. It was found that the voltage dependence on the applied gate current $V(I_g)$ showed a periodic dependence because this corresponds to the current generating an extra flux quanta in each loop of the JVFT. Also the curves of $V(I_g)$ shifted along the $I_g$ axis with increasing bias current because of the self field created by the bias current. Additionally, a current gain of more than 20 was found at temperatures below 60 K.

![Figure 96: Results from Gross et al. (a) Critical current versus gate current for an asymmetric JVFT of a parallel array of 10 junctions at 60 K. (b) The voltage versus gate current dependence for 670 μA (solid) and 600 μA (dotted) Tavares et al. [99] produced similar devices based on YBCO grain boundary technology. These had 10 or 20 junctions, with an inductively coupled control line. Again the $V(I_g)$ of the JVFTs showed a periodicity and shifting along the control current axis. These devices also produced showed a gain of between 8 and 40 at a temperature of 77 K.](image)
Bauch et al. [104] constructed a number of devices that used symmetric and asymmetric bias currents. They found that asymmetric JVFTs produced a gain of up to 30 at a temperature of 60 K. However, symmetric designs had a gain of a lot less. Schuler et al. [105] fabricated parallel arrays with one having a gate line parallel to the grain boundary and one with the gate line perpendicular to the grain boundary creating a so-called Josephson fluxon-antifluxon transistor (JFAT). This is shown in Figure 98.

Results of this experiment showed that the JFAT had a larger gain of 0.643 compared to 0.386 for the standard JVFT. There are two reasons for this; firstly the JFAT can be viewed as two parallel, asymmetric JVFTs. This causes the device to behave like the asymmetric devices discussed previously, increasing the gain of the device. Secondly, the placement of the gate line in the JFAT means that there is higher coupling between the gate line and the array.
3.2 Array Design and Fabrication

3.2.1 Simulations
To understand the differences in the behaviour between a SQIF and a parallel array of Josephson junctions, simulations were made for different array configurations. As stated previously SQIFs have an irregular grating structure and therefore it was necessary to incorporate a loop distribution that would provide an incommensurable distribution to avoid any $\Phi_0$-periodicity, while preventing $\Phi_0$-periodicity is not necessary for parallel arrays. As such, it was essential that some simulations of the voltage output $V_{dc}(B)$ were run using

$$V = \sum_{n=1}^{N} I_c R \sqrt{\left( \frac{I_B}{2I_c} \right)^2 - \left| \cos \left( \pi \frac{\Phi_n}{\Phi_0} \right) \right|^2}$$

(3.3)

where $\Phi_n$ denotes the flux passing through each junction in a summation of $N$ loops, $R$ is the resistance of the array, with $I_{ctrl}$ and $I_c$ being the bias and critical current respectively. Several different loop distributions were modelled, varying between logarithmic, exponential and arithmetic sequences.

Due to the area of the loop being proportional to the amount of flux contained by the loop it is possible to ascertain that for an arithmetic sequence the flux intersecting the $n^{th}$ loop is given by

$$\Phi_{arith}(n) = \frac{n}{N} \Phi_N$$

(3.4)

where $n$ is the $n$th loop and $N$ is the total number of loops. Consequently, the flux contained by the $n^{th}$ loop is a logarithmically distributed set of loops is shown to be

$$\Phi_{ln}(n) = \ln \left( \frac{n}{N} \right) \Phi_N$$

(3.5)

Furthermore, this can be extended to include the exponential sequence by simply replacing the logarithmic function with an exponential function, giving

$$\Phi_{exp}(n) = e^n \Phi_N$$

(3.6)
From these simulations it can be seen that the arithmetic simulation has an $N\Phi_0$-periodicity which is an improvement on the usual SQUID $\Phi_0$-periodicity if there are enough junctions used. Despite the limitations of this distribution, which for example gave an $N\Phi_0$-periodicity for the arithmetic distributions, a physical device would likely contain more variation in loop size due to imperfections in manufacturing processes. Thus, in reality the $N\Phi_0$-periodicity would likely vanish.

The exponential distribution $e^n$ and logarithmic $\ln(n/N)$ distribution provided a large delta-like trough with minimal noise as well as having no discernible $\Phi_0$-periodicity. However, it is important to note that the $\ln(n/N)$ distribution shows an exponential increase in noise with number of junctions. The other logarithmic distribution, $\ln(n)$, showed that despite having no $\Phi_0$-periodicity it also had a large noise component around the delta-like trough.

![Voltage response graphs](image-url)

*Figure 99: The voltage response of $e^n$, arithmetic, $\ln(n)$ and $\ln(n/N)$ loop distributions*
3.2.2 Mask Design

When considering the design of the SQIF a number of factors had to be taken into account such as $\beta_L$ and the $J_c$ so that an appropriate $V_{dc}$ characteristic could be created. Therefore it was necessary to calculate $\beta_L$ to give a suitable loop size. The inductance of the SQIF has two main components consisting of the hole inductance $L_{\text{hole}}$ and the kinetic inductance $L_{\text{kin}}$ which are given by

$$L = L_{\text{hole}} + L_{\text{kin}}$$

$$L_{\text{hole}} = 1.25\mu_0 h$$

$$L_{\text{kin}} = 1.25 \times 10^{-6} \frac{\lambda_{ab} 2l}{d w}$$

where $\mu_0$ represents the magnetic permeability, $h$ is the hole’s average side length, $\lambda_{ab}$ is the penetration depth along the ab plane, $d$ is the film’s thickness, $w$ is the junction width and $l$ is the junction lengths. The result of these calculations was that in order to keep the $\beta_L << 1$, the range in junction length was from 8μm to 13μm, with the junction width being 5μm. These calculations also formed the basis of choosing the grain boundary orientation of the bicrystal which is dealt with in section 3.4.3.

The performance of a SQIF depends largely on its configuration and whether it is connected in parallel, series or a combination of the two [86, 88]. When considering a combination of both serial and parallel connections it can be considered to be as a two-dimensional array with the serial parts forming $N$ rows and each row containing $M$ junctions in parallel [86].
Generally the voltage swing $\Delta V$ is proportional to the number of junctions, the trough width $\Delta B$ is inversely proportional to the number of rows. Conversely, the gain is proportional to the number of rows. Therefore careful consideration was required when deciding on the number of junctions and rows. Additionally, the voltage noise $\delta V$ is proportional to the square root of the product of the number of junctions and rows.

![Figure 100: An array with arbitrary loop sizes that consists of 4 rows of 14 junctions. The grain boundary is shown by the dotted line running through the centre of the device](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Single SQUID</th>
<th>Serial SQIF</th>
<th>Parallel SQIF</th>
<th>Parallel–serial SQIF</th>
<th>Serial–parallel SQIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_p$ ($\mu$V)</td>
<td>10</td>
<td>440</td>
<td>52</td>
<td>72</td>
<td>130</td>
</tr>
<tr>
<td>$B_{\text{in}}$ (nT)</td>
<td>450</td>
<td>360</td>
<td>190</td>
<td>407</td>
<td>340</td>
</tr>
<tr>
<td>$V_T$ ($\mu$V $\mu$T$^{-1}$)</td>
<td>70</td>
<td>2100</td>
<td>520</td>
<td>320</td>
<td>650</td>
</tr>
<tr>
<td>$\delta V/V_p$ (%)</td>
<td>–</td>
<td>18</td>
<td>12</td>
<td>16</td>
<td>23</td>
</tr>
<tr>
<td>$Z$ (Ω)</td>
<td>8</td>
<td>440</td>
<td>0.05</td>
<td>11</td>
<td>3</td>
</tr>
<tr>
<td>$B_n$ (pT Hz$^{-1/2}$)</td>
<td>8.1</td>
<td>2.0</td>
<td>5.0</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td>$f_1/f_2$ (Hz)</td>
<td>8</td>
<td>3000</td>
<td>30</td>
<td>15</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 1: Comparison of a single SQUID loop and different SQIF setups [88]

From Table 1, it can be seen that in all the majority of cases the SQIF out performs the single SQUID, with the serial SQIF seemingly the best option. However, it is also required that the device be reliable and given that the bicrystal grain boundary is very rarely completely homogeneous and any break would result in the device failing. Therefore it was decided that it would be preferable to incorporate some sort of parallel feature into the SQIF to increase reliability.
It should be noted that all designs incorporated a flux focussing structure called a pickup loop because $V_{dc}(B)$ can be significantly enhanced and noise reduced depending on the configuration of the SQIF. A serially connected SQIF is inductively coupled to the pickup loop while a SQIF connected in parallel is directly coupled. These can be seen in Figure 101 with figures pertaining to their performance in Table 2 below.

![Figure 101: Inductively coupled serial SQIF (left) and directly coupled parallel SQIF (right) [87]](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Single layer; inductively coupled</th>
<th>Single layer; directly coupled</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Serial SQIF</td>
<td>Regular SQUID array</td>
</tr>
<tr>
<td>$V_p$ ($\mu$V)</td>
<td>390</td>
<td>24</td>
</tr>
<tr>
<td>$B_{hw}$ (nT)</td>
<td>26</td>
<td>30</td>
</tr>
<tr>
<td>$V_0$ ($\mu$V nT$^{-1}$)</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>$V/V_p$ (%)</td>
<td>17</td>
<td>–</td>
</tr>
<tr>
<td>$B_0$ (ft Hz$^{-1/2}$)</td>
<td>190</td>
<td>225</td>
</tr>
<tr>
<td>$f_{1/f}$ (Hz)</td>
<td>3000</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2: Comparison of devices using inductively and directly couple pickup loops. Pick up loops were used to induce a screening current in the devices [88]

After finalising the limitations of the array, 18 different array masks (6 arithmetic, 6 exponential and 6 logarithmic loop distributions) were created with 9 repeats of the most important designs. In addition to these 4 types contact masks were produced and a frame mask, which was used to reveal the grain boundary.
The mask was designed using CleWin 3, a program specifically designed for making photolithography masks. This was used as opposed to AutoCAD 2010 after numerous problems with design conversion were encountered in the early phases of design.

Each design, although being slightly different, contained a number of repeating elements. Firstly, the corners of each mask contained squares which could be used to line up the mask over previous layers. Moreover, a chevron like pattern was introduced onto the mask along the middle of the mask to align the grain boundary with because this has to be precise within ±4μm. One of two types of pickup loop designs were used in each design, these being a single large pickup loop (5μm at its smallest point and 1000μm at its widest) and one that consisted of 20 small loops, one inside the other which were 5μm at their smallest and 20 at their widest.

Figure 102: SQIF masks for the different layers including the edge masks, contact masks and masks for different SQIF layouts.
Figure 103: Serial SQIF design with multi-pickup loops. It was hoped that this multi-loop design would be more effective than a large, single loop (left). Parallel SQIF design with directly coupled pickup loops (right)

3.2.3 Sample Fabrication

The operating properties of an array do not only rely on the structure of the array itself but also on the structure of the substrate and grain boundary as well as the quality of the thin film. The $I_c$ of the array is dependent on the quality of the grain boundary. As a result if this is high then the inductance parameter will be more than one. This will result in a drop in performance of the device due to increased noise and decrease in the voltage trough.

The way to ensure this does not happen is to change the angle of orientation of the two crystals. In general, the current-angle relationship varies logarithmically from a transmission probability of $\sim1$ when the crystal misorientation is $0^\circ$ to practically $0$ when there is a $45^\circ$ misorientation (this is even smaller if the crystals are asymmetrically arranged) [35].
Figure 104: Relationship between rain boundary angle and $j_c$. It shows that the $j_c$ is highly correlated to the angle of the grain boundary, with low misorientations producing high $j_c$ values, decreasing to values $10^6$ smaller at 45° [35].

Given this information, two SrTiO$_3$ bicrystal were sought, the first having a 30°, symmetrical orientation and the other one having being a 45° symmetrical orientation in the <001> plane. These were chosen as previous work by other teams had been carried out using 24° symmetrical substrates which had caused the inductance parameter $\beta_L$ to be greater than unity [91].

In recent years, there has unfortunately been a loss of knowledge in the industry which has led to a widespread shortage in good quality, homogeneous bicrystals. Despite the fact that the device would likely work on an inferior bicrystal, a lot of time was dedicated to sourcing bicrystals with homogeneous grain boundaries and these were eventually obtained from MTI Corporation, a supplier from the United States.

The quality of the thin film superconductor also dictates how well a device will work. Thus, it was also necessary to find a company capable of producing a good quality YBCO thin film, with minimal imperfections in the lattice structure. Theva GmbH, a highly recommended company in Germany, provided such a film which consisted of a 100 nm thin film of YBCO with a $T_c$ of 92 K and having a $j_c$ of 3.8 MAcm$^{-2}$. This can be viewed in the SEM image in Figure 105. A 200 nm layer of gold was also deposited to primarily provide contacts for the array later, but also to stop the YBCO oxidising.
In order to manufacture successful samples a number of issues had to be addressed. These included which method of etching to use and which photoresist would be appropriate for that method. A number of possible ways to etch the samples were then evaluated. These were plasma etching, chemical etching and ion beam milling.

Plasma etching was trialled as an alternative to ion beam milling as it is more prevalently used within industry and academia and thus the equipment is more easily accessible. One bicrystal sample was used to test the reliability and feasibility of this method. This was used to clear the edges of the sample, revealing the bicrystal boundary. An etch recipe was ascertained which consisted of a combination of \( \text{Cl}_2 \) and \( \text{Ar} \), both at 10 sccm each. This was maintained at a pressure of 5 mTorr and an RF power and LF power of 250 W and 750 W respectively. The rate at which the YBCO was etched using this recipe was estimated at 100 nm min\(^{-1}\).

However, it was found that there were a number of problems regarding this method of etching. Firstly, the etch rate of the YBCO was found to be considerably smaller than the etch rate of the photoresist. Therefore, a hard-mask layer consisting of \( \text{SiO}_2 \) had to be deposited. This meant that an intermediary layer of titanium also had to be deposited to guarantee adhesion between the \( \text{SiO}_2 \) and Au layers. These two additional layers were used to slow the etching rate of the photoresist. This greatly increased the complexity of the manufacturing
process because not only did the YBCO have to be etched but also the SiO₂ using a separate recipe, which consisted of CHF₃ and O₂ at 100 and 5 sccm respectively at a pressure of 50 mTorr and 150W of RF power and an etch for the Ti layer which was removed using HF and H₂O in a ratio of 1:10 respectively.

Moreover, the etch profile was also very inconsistent around the edge. Had this been an array of junctions it is not clear whether this profile would have caused failure of the device. In addition, after etching carbon compounds were deposited onto the etched surface which was likely caused by pyrolysation of the grease used to attach the sample to the stage. Pyrolysis of the grease probably occurred because of the highly aggressive nature of the etching process needed for YBCO. It may have also led to the YBCO film being damaged. These faults can be seen in Figure 106. Due to these problems, this method was disregarded.

![Figure 106: Sample after plasma etching. It can be seen that there is an uneven etch, with dark deposits of a carbon compound around the edge of the sample](image)

Chemical etching was also tested as a method of etching. This used a saturated solution of EDTA to preferentially etch the barium. This was used to etch the edge of the other two samples revealing the bicrystal boundary. Obviously for such a large area this is an ideal method. However, the reliability of chemical etching was questioned because of the possibility of undercutting could cause the junctions to fail. This being the case, it was discarded when etching the finer structures of the device.
Therefore, ion beam milling was chosen to etch the main structure of the device. Primarily this was used because this method is the most commonly used method when etching high temperature superconductors. However, due to constraints on the mask aligner at Birmingham University, which only used 3 inch x 3 inch masks, it was required to perform the spinning and development of photoresist at Nottingham University.

Before etching the YBCO samples, the photoresists in Nottingham needed to be tested with the ion beam miller at the University of Birmingham. In order to do so a number of dummy samples were created which consisted of a piece of silicon wafer with a number of different photoresists spun on, these being BPRS 100, BPRS 150 and AZ6612. Some step profiles were created by exposing areas for various amounts of time. These were then measured using both AFM and laser interferometers. AFM measurements of this film were unsuccessful because of the large areas involved in the measurement and the fact that AFMs can only scan ~10 µm² at a time. The laser interferometer measurements on the other hand, showed some interesting results. They presented an interference-like profile of troughs, where the ions had removed material, and peaks where the photoresist had remained un-etched on the surface of the sample and is shown in Figure 107. This can only be explained by having the beam scattered by Fresnel diffraction because the tin foil was not perfectly flat against the surface and so acted like an aperture.

Following this it was decided that it would be easier to produce dummy samples using the final structure designs again consisting Si wafers with differing photoresists on, but his time they had been developed. These could then be used to discover whether the resists would last the milling process, especially around the junctions. Milling of these samples took place for 20 minutes because it was well known that the etching rate of YBCO is ~10 nm min⁻¹, therefore for a film of 150 nm thick it would take 15 minutes. Thus, it would be certain that the photoresists would last the entire milling process. Interestingly all photoresists remained undamaged around the pickup loops and contact areas. Nonetheless, it was found that BPRS 150 remained completely intact around the junctions, while there was some degradation within the other photoresists around the junctions. Therefore, BPRS 150 was used in the processing of the final structures.
Figure 107: 3D micrograph (top) and laser interferometer (bottom) measurements of BPRS 150. It showed an interference-like pattern. Similar results were found with BPRS 100 and AZ6612

Prior to using the ion milling beam at the University of Birmingham it was necessary to carry out work to prepare the Au contact layer. Obviously, milling through both the YBCO and Au layers would add to the complexity of the milling process because this would not only the increase time needed for the etch, which could cause the photoresist to fail but also it would cause a larger shadow in the beam which would change the geometry of the junctions significantly. Consequently, it was decided to create the Au contacts first. To do this, two stages were required. The first stage involved etching the entire device including the array structure, pickup loops and contacts into Au layer using an Au-chemical etch consisting of a KI : I₂ : H₂O mixture with a 4 g: 1 g: 40 ml ratio. The array structure and pickup loop could then be removed in a further etch leaving the Au contacts correctly positioned. A further benefit of this method is because the bicrystal boundary is easily viewed through the Au, even with a layer of photoresist 1.2 μm thick on top of it meant that these could be used to align the YBCO photoresist layer.
Following this, the samples could be milled. The etching rate of YBCO under ion milling is well known to be $\sim 10 \text{ nm min}^{-1}$ at an angle of 45°, depending on the energies involved. Therefore, it was a simple process of inserting the samples into the beam and milling for 15 minutes. The results of this etch can be seen in figure 3. It should be noted that at this stage, photoresist was still covering the structure hence the homologous look to the sample.

After milling the YBCO samples, they were mounted on sample holders. Unfortunately, the bonding machine used to ultrasonically bond gold wires between the sample and sample holder is currently broken. Nonetheless, the required part should be available in the near future.

After the samples were milled, acetone was used to remove the remaining photoresist in an ultrasonic bath. This also had a secondary effect of beginning the cleaning phase. The sample was then put through further baths of methanol and isopropanol that removed any remnant photoresist and erroneous debris from the milling process.

Following this the sample was glued to a test bed using low temperature vanish. To create a four point contact three methods were trialled. These were ultrasonically bonded gold and silver wires respectively; and gold wires attached using silver paste. It was found that the ultrasonic bonds for both silver and gold wire were unreliable and broke when cooled. Instead the contacts were made by means of 10 μm gold wire and silver paste with 2-butoxyethyl acetate as the solvent.
The existing sample holder had to be modified so that an electromagnet could be fitted to provide a $B$-field up to approximately 4 mT. A wire was run from a spare I/O port on top of the flange, through the baffles to the magnet. This supplied power to the magnet, which was then earthed through the sample holder itself. Current and voltage leads were also jumped from the existing sample holder to the new holder and held in place using silver paste.

Once the sample had been prepared and inserted into the cryostat it was evacuated using a combination of rotary and turbomolecular pumps to obtain a pressure of $\sim 10^{-5}$ Pa with a few mbar of He gas added to act as a transfer gas. The instruments were then connected as shown in Figure 109: Experimental setup while measuring the parallel array of junctions. Using the electromagnet allowed small magnet fields to be applied to the device and the compressor started. After starting the compressor, an $RT$ measurement was taken as the sample cooled using a LabVIEW $RT$ measurement program. A sampling rate of 0.5 seconds was used as this would ensure sufficient data points over the transition temperature. A bias current of 100 $\mu$A was used as this would guarantee that there was negligible sample heating while also negating any noise from the measurement.

$IV$ characteristics were also taken. These were used to analyse the $V_{dc}(I_{ctrl})$, $I_{dc}(I_{ctrl})$ and resonant behaviours of the device. These were also used to calculate the maximum gain, $g_{\text{max}}$. The $V_{dc}(I_{ctrl})$ characteristics were analysed by setting a series of current criteria where there were large differences in the voltages. The voltages could then be plotted against the applied magnetic field current. Interpolating a further 1700 points within this data set allowed a smoothing algorithm to be applied.

The $I_{dc}(I_{ctrl})$ characteristics were also analysed in a similar way. However, in this case voltage criteria were chosen where there were large differences in the output current. These were also interpolated upon with a further 1700 points and smoothed, before being plotted. These were used to investigate the magnet current values that produced the highest gain. By finding areas of the $I_{dc}(I_{ctrl})$ characteristic with large gradients, it was reasoned that these would be the areas most likely to have the highest gain. The $IV$s for these magnet current values were then systematically searched through to find ones that had the largest difference in current outputs. This value divided by the change in the applied current to the magnet gave the maximum gain $g_{\text{max}}$. 

150
3.3 Experimental Results

3.3.1 $RT$ Measurements
During the cooling phase it was found that initially the $T_c$ was recorded at 86 K and 93 K when the sample was being cooled and heated respectively, shown in Figure 110. This approximately the equal to the known value of 92 K found by Theva.
3.3.2 IV Measurements and Flux Flow Resonances

Current-voltage characteristics were also taken across the parallel array, for temperatures ranging from 89 K down to 4.7 K. From the measured IV’s it was calculated that each individual junction’s critical current, $I_c$, was approximately 3 μA and $I_cR_N$ product of about 50 μV at 77K. This translates to a Josephson critical current density $J_c$ of approximately $1 \times 10^3$ A·cm$^{-2}$.

Generally the IV measurements displayed a number of features which were of note. Firstly, the $I_c$ of the system varied greatly with different temperatures and applied magnetic fields. Secondly, there appeared to be several current resonance features in the resistive state. At temperatures close to $T_c$ the resonances appeared to be approximately the same size as the $I_c$ itself. The size of these resonances remained relatively constant as the temperature decreased, although the relative size compared to the $I_c$ obviously decreased quite dramatically.
These resonances are obviously flux flow resonances [108], since they appear to freely flow up and down the IVs. These are caused by a chain of, or individual, Josephson vortices moving up and down along the array and interacting with individual junctions. To clarify the physical origin of the resonances, it is helpful to recall a mechanical analogue of the system. The Josephson junction array may be viewed as the a chain of $N$ identical pendulums, each of which is viscously damped and free to move transverse to the axis of the chain, driven by a constant torque, and coupled to its nearest neighbours by torsional springs. A vortex corresponds to a kink (soliton) propagating along the chain. In this configuration, a given pendulum hangs almost straight down for much of the time, but when the kink passes by, the pendulum overturns rapidly and oscillates for the period between passing kinks. These oscillations are the analogue of the $EM$ radiation excited by the kink. A resonance occurs if the pendulum oscillates precisely an integer number of times ($m$) between successive passages of the kink; or equivalently, when the vortex lattice moves at the same velocity as one of the modes $m$. The possible oscillation frequencies are the lattice eigenfrequencies of
small oscillations about the kink. Each junction (pendulum) has an identical behaviour except for a constant shift in time. This suggests that the solutions are well approximated by travelling waves.

The resonances can be seen in Figure 112 where $IVs$ taken at 89 K show the voltage position of the resonance is clearly decreasing. Further resonances become even more obvious when the derivative $dI/dV$ or conductance is calculated.

![Figure 112: (a) A family of 8 IVs taken at 89 K and (b) $dI/dV$ of the IVs, which have each been shifted vertically above one by another 25 Ω$^1$ for clarity. The arrows show the direction of motion for the flux flow resonances with increasing.](image)

The $IVs$ also show the voltage gap between each resonance is periodical, starting at 0.15 μV and increasing to 0.78 μV, before resetting to 0.15 μV. This can also be seen in Figure 113 where the bunching of the resonances is more obvious.

Figure 113 shows the voltage position of the resonances are quasi-periodic with applied magnetic field. The primary resonance, $m = 1$, seems to be periodic with positive voltages where it reaches a maximum value every 1.8 mA or 12 μT. Further resonances, $m = 2$ and $m = 3$, were found to have some repeating features, though they cannot be described as periodic as such. Moreover, $m = 2$ and $m = 3$ also appear to be symmetrical with each other about 1 μV.

Analysis of lower temperatures showed that more resonances were produced suggesting that more Josephson vortices were able to penetrate the junctions of the device with decreasing
temperatures. The behaviour of the resonances also became more chaotic, since some resonances were found to be stationary (i.e. Shapiro steps) while other flux flow resonances were seen to merge together and separate. Nevertheless, the resonance \( m = 1 \) remained present throughout all the analysed temperatures.

![Graphs showing voltage positions for different magnetic field values](image)

Figure 113: (a) The voltage positions for \( m=1 \). This has a distinct periodic function. (b) The voltage positions for \( m=2, 3 \) which have some repeating features and have some symmetry around \( y = 1 \) μV

### 3.3.3 \( V_{dc}(I_{ctrl}) \) Measurements

Plotting the voltage against its corresponding \( B \)-field value, at set current values revealed the \( V_{dc}(I_{ctrl}) \) dependency. The output was similar to that of a SQUID; this being periodical and symmetrical. Similarities to a diffraction pattern, created by an optical diffraction grating consisting of multiple slits, were obvious. It was found that close to \( T_c \) it had a periodicity 1.8 mA or 12 μT, and this also corroborates the periodicity found for the flux flow resonances. The results for 81 K and 89 K are shown below in Figure 114.
Figure 114: $V_{dc}(I_{ctrl})$ of parallel array at (a) 81 K where the current criteria ranged between 1.00 mA and -0.98 mA and (b) 89 K where the current criteria ranged between 500 μA and -495 μA. These display the periodic nature of the device when the temperature is close to $T_c$. The period was found to be 1.8 mA or 12 μT.
$V_{dc}(I_{ctrl})$ look qualitatively different for positive current bias relative to negative current biases. This is due to the asymmetric loop configuration within the array as investigated in detail in reference [109].

To ensure trapped flux was kept to a minimum the parameter $\beta_L \ll 1$ where

$$\beta_L = \frac{2\pi LI_c}{\Phi_0}$$

(3.10)

and

$$I_c = j_c \cdot w \cdot l$$

(3.11)

This limited the maximum length of the loop to 13 μm, giving a maximum area of 39 μm$^2$. A further limitation was imposed on the minimum length of the loops, this being 8 μm, because this would allow minor errors in the alignment of the junctions across the grain boundary. However, designs from other groups such as Schultze et al. [89] had junctions that had a much larger range, in some case the largest being 100 times larger than the smallest. Nevertheless, these devices suffered from excessive flux trapping. It should also be noted that the $V_{dc}(I_{ctrl})$ curve at 87 K seems to behave non-periodically, with the peaks suppressed probably because of flux trapped within the junctions.

As the temperature was decreased this periodicity was lost, which is seen in Figure 115. This is because as the temperature decreases the $\beta_L$ parameter of each loop became more important and non-negligible. This created large asymmetries in the amount of self-induced flux over the entire device which resulted in the symmetrical voltage dependency, found at higher temperatures, to break down.
3.3.4 $I_{dc}(I_{ctrl})$ Measurements

Current-field measurements, $I_{dc}(I_{ctrl})$, were also analysed to determine the gain of the device when varying magnetic fields were applied to the device. The maximum gain of this device was calculated by searching through consecutive $IV$s for large differences in the critical current that correspond to a small change in $I_{ctrl}$. Once the largest difference in outputs was found it was a simple task of using equation 3.12 shown below.

$$g_{max} = \max \left( \frac{\partial I_c}{\partial I_{ctrl}} \right)$$  \hspace{1cm} (3.12)

It was found that the gain of the device was small when the temperature was close to $T_c$. This then gradually increased to a maximum at 77 K and decreased again as the temperature decreased down to 4.7 K.

At 89 K, the function of $I_{dc}(I_{ctrl})$ was very periodic with a periodicity of 1.8 mA. This matches the value found previously when measuring the voltage response of the device. This periodicity was then lost at lower temperatures. The reason for this is that when operating close to $T_c$, $\beta_L$ is considered negligible and does not have any effect on the $I_c$. Instead the output is periodical with each maxima representing an additional flux quanta penetrating each loop.
Figure 116: $I_d(I_{ctrl})$ at 89 K for voltage criteria ranging between -2.5 μV and -7.5 μV. This shows that at temperatures approaching $T_c$ periodicity of the device is maintained.

$I_d(I_{ctrl})$ measurements performed at 84 K had no real periodicity, which was not unexpected given that flux was thought to be trapped while measuring $V_{dc}(I_{ctrl})$ at the same temperature. Nevertheless, the results showed that there was a large gain at several applied currents with the largest average gain, which is calculated over a large variation in magnetic field current, was found to be 0.17 and 0.64 for positive and negative voltage criteria respectively.

However, the maximum gain, $g_{max}$, which is calculated from the gain in two consecutive measurements with a change in control current $I_{ctrl}$ of 15 μA, was found to be 17.33 ± 0.02 and was found when the current was negatively biased and $I_{ctrl}$ was around 1.8 mA.
Figure 117: (a) $I_{dc}(I_{ctrl})$ at 84 K for voltage criteria ranging between -250 nV and -2.5 μV. This shows asymmetrical and irregular behaviour with regards to the applied magnetic field current. (b) $G_{max}$ calculated at 84 K. This showed a maximum gain of $17.33 \pm 0.02$ when the device was negatively biased.

At 81 K the $I_{dc}(I_{ctrl})$ retained its periodicity for positive voltage criteria of 1.8 mA applied across the coil. However, there were large differences in the maximum amplitude between the first and second period when positive voltage criteria were used. When a negative voltage criterion was used it was found that this periodicity was not entirely lost, with the large peaks being shifted relative to the peaks found when using a positive voltage criterion. There were also smaller peaks in between that displayed switching behaviour. The average gain found for this temperature was 1.55 and 1.16 when using positive and negative voltage criteria respectively.

Figure 118: (a) $I_{dc}(I_{ctrl})$ at 81 K for both positive voltage criteria between 250 nV and 2.5 μV showing quasi-periodic behaviour. (b) $G_{max}$ calculated at 81 K. This showed a maximum gain of $14.50 \pm 0.02$ when the device was positively biased.
$G_{\text{max}}$ was found to be $14.50 \pm 0.02$ at 81 K when the device was positively biased and the magnetic current was around 1.3 mA or 8.6 μT. Although this is slightly smaller than the measurements at 84 K, it is still a high gain compared with those found at much lower temperatures.

The results of $I_{\text{dc}}(I_{\text{ctrl}})$ measurements at 77 K showed the only set of measurements where both negative and positive voltage criteria showed periodicity of 1.8 mA. When taking a positive voltage criterion, two distinct peaks were observed, with one having a much larger amplitude than the other. Using a negative voltage criterion resulted in these peaks being shifted and smaller peaks being observed between the main structures. Since this also happened in the previous measurement it seems that this is indicative of the device’s asymmetric behaviour. It is a result of the bias switching from negative to positive causing the configuration of the junctions to change. These measurements also showed an average gain of 2.61 for negative voltage criteria and 5.00 for positive voltage criteria.

The value of $g_{\text{max}}$ at 77 K was calculated to be $19.28 \pm 0.03$ when positively biased and a $I_{\text{ctrl}}$ current of around 1.3 mA was used. This produced the largest gain of any of the measurements.

Measurements of the $I_{\text{dc}}(I_{\text{ctrl}})$ characteristics at 57.5 K showed no periodicity. This is likely due to the device no longer operating in the low inductance limit, where self-field effects
become more prominent, such that the $I_c$ is affected. From this point on no sign of periodicity within the $I_{dc}(I_{ctrl})$ measurements was found.

Nonetheless, average gains of between 0.42 and 5.51 were achieved for temperatures ranging from 57.5 K to 4.7 K. However, there was no relationship between the temperature and the average gain.

![Figure 120](image)

Figure 120: (a) $I_{dc}(I_{ctrl})$ at 57.5 K for voltage criteria ranging between 1 μV and 12.5 μV showing it is non-periodical with regards to the applied magnetic field current. This suggests that at temperatures around this value $β_L$ components become more important to the dynamics of the device. (b) $g_{max}$ was found to be 15.66± 0.02

Additionally, measurements of the maximum gain at low temperature within the device seemed to decrease with temperature. This is shown by gains ranging from 4.38 ± 0.05 at 4.7 K to 15.66 ± 0.02 at 57.5 K. This decrease may have been due to the control current being altered by larger amounts, since measurements between 77 K and 89 K used a $ΔI_{ctrl}$ value of 15 μA, whereas measurements for 57.5 K used 40 μA and measurements between 4.7 K and 30 K used 100 μA.
Figure 121: $g_{\text{max}}$ for temperatures of (a) 30 K, (b) 10 K, (c) 7 K and (d) 4.7 K.

The behaviour of $g_{\text{max}}(T)$ was extremely asymmetric with high gains as high as 19, close to $T_c$. While the gains decreased dramatically to as low as 4.387 once the temperature decreased. These results are discussed further in Chesca et al. [110].
Figure 122: Temperature dependence of $g_{\text{max}}$. This shows a maximum gain at 77 K.

3.4 Conclusion

A superconducting array of parallel Josephson junctions has been developed based on YBCO thin film bicrystal grain boundary Josephson junctions (GBJJ). This consisted of 22 groups of 20 junctions to create a total of 440 junctions. After much development the device was fabricated using standard photolithography processing and a mixture of chemical etching and ion beam milling.

A number of measurements were used to characterise the device, including $RT$, $IVs$, $V_{dc}(I_{ctrl})$ and $I_{dc}(I_{ctrl})$. This showed at $T_c$ of 86 K when cooling and 92 K when heating. Families of $IVs$ at different applied magnetic field values were also taken and used to calculate a variety of characteristics. Firstly, flux flow current resonances were found within most $IVs$ that appeared to shift, with respect to the voltage value which suggests that the device was operating in a flux-flow mode. Analysis of the $IVs$ at 89 K showed that the gap between the major resonance began at 0.15 $\mu$V and increased to 0.78 $\mu$V before resetting to 0.15 $\mu$V. This was caused by the differing inductances within each group of 20 junctions, which caused either high or low damping within the system, depending on their direction. Moreover, the different sets of resonances appeared to be periodical with respect to the magnetic field.
applied via a control current. Additionally, it was also seen that below 77 K these resonances became aperiodical. Decreasing the temperature below 77K leads to a decrease in the losses experienced by moving fluxons (i.e., smaller damping) accompanied by an increased discreteness of the array (the discreteness parameter is $(\beta L)^{1/2}$). At some threshold temperature, $T_{th}$, numerical simulations show that flux-flow resonances are completely suppressed and a transition to a chaotic regime occurs. Consequently, in our case for temperature below $T_{th}$ (which appears to be around 77K) the switching behaviour and the high gains associated with the flux-flow resonances both vanish.

$V_{dc}(I_{ctrl})$ was also measured using the $IV$s. This showed periodical behaviour at temperatures close to $T_c$. These had a periodicity of 1.8 mA or 12 μT. This means that an extra flux quantum enters every loop every 1.8 mA that was applied through the coil. It is thought that because the loop sizes were similar it caused the output to be periodic.

Nevertheless, keeping the junction and loop widths the same resulted in unexpected behaviour, with the device operating as a Josephson vortex flow transistor (JVFT) which produced gains as high as $19.28 \pm 0.03$ around 77 K. However, these gains decreased dramatically as temperature decreased below 77 K. In addition, switching behaviour was also found which is explained by a transition from a state where the entire group of 440 Josephson junctions are completely disordered to one in which the junctions are highly ordered. Therefore, the record high current gains found at 77 K and above as well as the switching behaviour make this device highly suitable for applications as a superconducting transistor. Further discussion of these results can be found in Chesca et al. [109, 110].
Bibliography


Appendix: Electric Transport Measurements of GdBa$_2$Cu$_3$O$_{7-\delta}$

Abstract

As a preface to working with the bicrystal samples described in chapters 2 and 3, it was necessary to practice the techniques involved in fabricating and measuring electric transport properties of superconducting samples, including mask design, sample preparation and measurements in a cryostat as well as calibration of the cryostat itself. As such, the first aim of this experiment was to evaluate the processing methods that may be used when fabricating arrays of Josephson junctions. The second aim was to measure both the transition temperature $T_c$ and the critical current $j_c$.

To this end, a sample of GdBa$_2$Cu$_3$O$_{7-\delta}$ (GBCO), a relatively new cuprate, was chosen because it had well known electric transport properties, such as a critical temperature of 91.5K and a critical current density $j_c$ of up to 4 MA·cm$^{-2}$ at 77 K [16]. Furthermore, it had a similar composition and structure to YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) and therefore had similar physical properties, enabling easy selection of substrate. It was constructed on a single crystal substrate of SrTiO$_3$ (STO) using pulsed laser deposition.

The results found showed the sample had a $T_c$ of 92 K. However, due to errors made in the etching of the sample and within the code for the current-voltage characteristic program, the $j_c$ was unable to be calculated.

Experimental Method

Mask Design

In order to evaluate and become accustomed to the different software used for mask designs, a test mask was created for use on the GBCO sample. The mask itself was a rudimentary design consisting of a number of single and double bridges, which ranged in size from 1μm to 50μm and 1μm to 100μm respectively. These led to electrical contacts at the edge of the sample which had a minimum size of 150μm to allow bonding to occur easily. The contacts alternated in length so that individual bridges could be recognised without zooming in and out on the sample during bonding.

Originally the designs were created in AutoCAD 2010. However, when these designs were converted into the machine code there were errors in the conversion. This meant that another
program had to be used, namely CleWin 3. CleWin 3 is a more fundamental program than AutoCAD 2010 but was designed specifically for the purpose of designing photolithography masks.

Figure 123: The bridge mask for the GdBa$_2$Cu$_3$O$_7$ thin film sample had a combination of single and double bridges

Figure 124: Single bridges on the mask which ranged in size from 1 μm to 50 μm
This research was used to inform the decision to use CleWin 3 to create the Josephson junction array designs in chapter 3 because of its ability to produce files compatible with the equipment used in industry.

**Sample Fabrication and Preparation**

The experiments within this chapter were conducted on a high temperature superconductor cuprate, namely GdBa$_2$Cu$_3$O$_{7-\delta}$ (GBCO) and were obtained from Marat Gaifullin and were fabricated in Japan. Typically, these were grown using pulsed laser deposition (PLD) on STO substrates because STO has a similar lattice parameter to GBCO, these being 3.905 Å for STO [53] and $a = 3.84$ Å and $b = 3.82$ Å for GBCO. This would ensure that the thin film was only placed under a small amount of tensile strain once it had been deposited.

The thin film was then cleaned using the standard cleaning process of placing the sample in an ultrasonic bath of acetone, then methanol and finally IPA to remove any impurities. To ensure good conductivity between the sample and the contacts a further Au layer was deposited ex-situ via evaporation. This was accomplished by firstly calculating the mass of Au shot needed to cover the GBCO in a layer 100nm thick, after which the Au shot was loaded into the chamber. Upon evacuating the chamber down to $10^{-5}$ mbar the Au shot was raised to its vapour pressure, coating the GBCO. The sample was then cleaned again using the standard process to remove any impurities from the surface before the resist was applied.

The next few steps were carried out by Loughborough University’s Mechanical Engineering Department. Here, the resist was applied to the film by spin coating. A viscous solution of photoresist was the applied to the surface of the film and spun rapidly at 5000 rpm for 40 seconds. This produced a layer approximately 1 μm thick. After spin coating the resist it was
placed on a hot plate at 90 °C for two minutes. This allowed the resist to harden while preventing the film from being heated for too long, which could have caused a loss of O₂ within the GBCO.

For e-beam etching, the photomask file was converted into machine code that was readable by the e-beam system. From there, the e-beam patterned the resist and underlying film. As seen in the figures below, the patterning process went awry which shows that the e-beam was incorrectly calibrated causing the top and bottom of the bridges to shift and be misaligned. This calibration error was due to the sample and mask being too big for the mask aligner, the mask itself had to be broken into several pieces when uploaded into the e-beam system. When the mask was reassembled an error in the machine resulted in it being distorted.

Moreover, when the resist was applied, excess resist was not removed causing bubbles of it to remain in the corners of the sample, which meant that there was an inhomogeneous etching rate across the sample. The result of this was that while the centre of the sample was etched fully, in some cases there was no GBCO film left, the edges had not been etched down to the substrate leaving an inhomogeneous film, rather than bridges, with multiple current paths to the contacts. This inhomogeneous etching rate and the misaligned bridges meant that the current path was not able to be determined and therefore the \( j_c \) could not be calculated.
Nevertheless, the photoresist was removed using the standard cleaning process and attempts at bonding were made so that resistance-temperature (RT) measurements and current-voltage (IV) characteristics could be taken. However, attempts at ultrasonic bonding proved unsuccessful because the gold contacts on the GBCO were found to peel off. It is thought that this is a result of the Au layer being deposited ex-situ, meaning that the adhesion properties between the GBCO and the Au layer were very poor. Owing to this, contacts were made by bonding Au wire directly to the GBCO layer using Ag paste.

**Filling the Cryostat**

To perform transport measurements at low temperatures, the cryostat’s reservoir first had to be filled. To fill the cryostat from room temperature the needle valve, which regulates the amount of liquid nitrogen allowed into the variable temperature insert (VTI), had to be flushed with helium gas to prevent it from freezing while the liquid nitrogen is pumped into
the reservoir. The reservoir could then be filled from the Dewar flask. If the cryostat was filled when it was still cold then the liquid nitrogen could be simply pumped into the reservoir.

When filling the cryostat with liquid helium the system first had to be filled with liquid nitrogen as described above. This was then removed using helium gas and liquid helium pumped into the primary reservoir. The secondary reservoir was filled with liquid nitrogen to provide a thermal shield to the helium bath.

To provide accurate data for a sample, both the $RT$ measurements and $IV$ measurements needed to be carried out in the same run; otherwise the results would be distorted by external factors such as the thermal contractions of the bonds. This meant that an $RT$ measurement needed to be run when cooling the sample; then an $IV$ measurement taken when the sample had been cooled below its $T_c$ and was at a stable temperature. Another $RT$ measurement could be conducted during the heating phase to provide the hysteresis of the sample.

### Resistance-Temperature Measurements

Resistance-temperature measurements required lowering the sample holder slowly into the VTI and controlling the temperature gradient in such a way so that the rate of decrease in temperature experienced by the sample was no higher than 0.1 K·s$^{-1}$. This precaution was observed to prevent any bonds from breaking. The temperature gradient of the VTI could be controlled via the amount of liquid nitrogen the needle valve lets in, the level of pumping applied to the system and the heating applied by means of the VTI heater. The resistance and temperature were recorded every second via a program created in LabView. The heating cycle simply involves raising the sample to a suitable level and setting the heater to 150K, so that the liquid nitrogen boils off and leaving it over night. It was important to observe both a cooling and heating measurement since it would allow the observation of any hysteresis within the measurement.
Using these methods meant a stable temperature of 65 K could be obtained, which is well below the boiling point of nitrogen (77.36 K). However, it was a necessity that the temperature did not fall below 63.15 K, the melting point of nitrogen, so that the cryostat was not damaged. While lowering the sample, it is also required that the pressure be kept constant at 20 mbar. This is however quite difficult due to the difference in temperature between the sample and the liquid nitrogen because of the latent heat of the sample holder, vaporising the liquid nitrogen when it gets close to the surface. This causes massive increases in pressure, which affect the outcome of the measurement. Nevertheless, the effects of these pressure increases can be minimised by lowering the sample far enough before it reaches its $T_c$.

A normal metal will behave in a linear manner with varying temperature. However, $RT$ measurements of superconductors will consist of a linear behaviour above $T_c$ and a substantial decrease in resistance upon reaching $T_c$. Also, there is some hysteresis between the cooling and heating cycles because of the latent heat of the sample holder. Therefore, the average of the cooling and the heating cycles should be taken to give an accurate result for the critical temperature. Furthermore, application of a magnetic field will result in the lowering of the critical temperature.
Current-Voltage Measurements
When the temperature had stabilised, $IV$ measurements could be performed. Obviously for this measurement to be taken the temperature had to remain invariant. This meant that it had to be achieved in as little time as possible and was accomplished by changing the timings on the current meter from a slow sweep to a medium sweep. A fast sweep was not used because multiple voltages were registered for each current value, resulting in an extremely noisy measurement.

For a normal metal this would obviously exhibit ohmic behaviour. Type I superconductors would be seen to have a supercurrent $I$ with zero voltage, until $I > I_c$, driving the material into a normal state. Type II superconductors exhibit slightly different behaviour due to their ability to allow flux to penetrate them. Up to $I_c$, type II superconductors show the same behaviour as type I superconductors. Upon reaching this limit the Lorentz force and the pinning force are in equilibrium (a state known as flux creep) and this can be seen in the non-linear behaviour of the $IV$ measurement [1]. If the current is increased further, such that $I > I_c$, then the Lorentz force would become bigger than the pinning force of the vortices causing the vortices to be dislocated from their locations (known as flux flow) [1]. At this point the material enters the normal state. From this we can see that the critical current is simply a measure of the force with which vortices are pinned to energetically favourable sites. Due to this, applying an external magnetic field can be seen to decrease the $I_c$ of the material.

Results
The sample was prepared using $e$-beam lithography. However, as stated previously there were a number of problems that were encountered during the etching phase. Therefore, rather than measuring the bridges’ characteristics the samples were used to take $RT$ and $IV$ measurements of the sample as a whole, despite not knowing the actual path the current was taking. This meant calculation of the $j_c$ was impossible.

A number of resistance-temperature measurements were taken to measure the transition temperature $T_c$ of the GBCO sample. The first $RT$ measurement, shown in Figure 128, was taken with no applied field and used a bias current of 100 μA. Using a bias current with this value meant that the signal measured was above thermal noise, while preventing any excessive Joule heating of the sample.
The sample displayed an obvious transition onset at 93.2 K. This concurred with the widely held value of 91.5 K. Additionally, the resistance decreased from a value of 7.5 Ω, just prior to transition, to virtually zero over a range of 7.7 K. However, upon heating, the contacts broke away from the surface and therefore the sample was removed and the contacts repaired.

A second $RT$ measurement was conducted once the sample’s contacts had been repaired. The cooling measurement showed a $T_c$ of 86.5 K and occurred over a range of 6 K with a decrease in resistance of 4.6 Ω. This value is obviously less than the 7.5 Ω from the first measurement and can be explained by the contacts being changed. Upon heating the sample, the transition began at 87 K, therefore the sample shows a small amount of hysteresis. The small amount of hysteresis is probably due to a thermal gradient between the sample and the temperature sensor.

It was also seen that there was a large difference of 1.57 Ω between normal states of the cooling and heating curves. This discrepancy could be the result of the Ag paste not being fully dry before cooling. During the cycling of the sample it may be possible for some of the thinner to evaporate causing a reduction in the overall resistance.
Moreover, there appears to be some distortion in the normal state resistance of the sample when both cooled and heated, which ideally would remain linear and behave according to Ohm’s law. The probable cause of this is thought to be the changes in pressure of the nitrogen in the VTI during both heating and cooling phases.

As well as $RT$ experiments, an attempt at $IV$ measurements was also made. However, results of the $IV$ measurements had varying degrees of success. Initially a measurement was conducted at 127 K, while the sample was still in its normal state. The result showed typical ohmic behaviour, with a resistance of 8.8 $\Omega$. This was approximately the value that was expected at this temperature according to Ohm’s law. This was used to check the contact ohmicity and also that the $IV$ program was running correctly.
However, measurements in the superconducting state were found to be inconclusive as the graphs showed behavior that was contrary to the typical superconducting $I\!V$ characteristics. This was found to be an error in the code that placed a limitation on the current of ±1.5 mA. This was so that the power consumption would not exceed certain levels which would have been desirable if the properties of devices were being measured. However, as this was a thin film specimen more power was needed to drive the sample into its normal state. This fault was only discovered after the sample had been removed from the cryostat and was therefore only resolved for measurements in chapters 2 and 3.

**Conclusion**

In conclusion, it was found that the transition temperature of GdBa$_2$Cu$_3$O$_{7-\delta}$ was found to be around 92 K which concurs with the widespread value found in literature of 91.5 K [16]. The transition occurred over a range of 5K suggesting that the film was of good quality. However, due to a number of errors, including an error in the code of the $I\!V$ program and an error in the processing of the sample causing an inhomogeneous thin film, it was not possible to find the $j_c$. 

![Graph showing current-voltage characteristics of the GBCO sample in its normal state at 127 K. This shows near-perfect ohmic behaviour.](image)
Nevertheless, the work completed in this chapter allowed informed decisions to be made in later chapters, particularly those involving sample processing methods and mask design. Moreover, this not only allowed the cryostat to be calibrated but more importantly allowed the user to gain more experience when running the cryogenic systems and fabricating samples.