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Abstract

Organic superconductors, discovered in 1979, continue to be of immense interest in condensed matter physics because they provide a clean realization of low dimensional electronic systems in which kinetic and potential energies are finely balanced. Of particular interest in our context is the need to reconcile contradictory evidence regarding the symmetry of the Cooper pair wave function.

High resolution microwave spectroscopy has been used to carry out electrodynamic measurements on single crystals of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and $\kappa$-(BEDT-TTF)$_2$Cu(SCN)$_2$. Cavity perturbation measurements were carried out at a frequency of 2.91 GHz at temperatures down to 0.1 K. A microwave magnetic field was applied perpendicular to the conducting planes to induce in-plane screening currents. In both materials, measurements of superfluid density reveal clear regimes of linear temperature dependence at intermediate temperatures with crossovers to higher-order power law dependence at low temperature. This result is consistent with $d$-wave superconductivity in the presence of strong disorder.
To my parents for believing in me.
To my husband for helping me believe in myself.
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Chapter 1

Introduction

From the time Heike Kamerlingh Onnes first discovered superconductivity in mercury in 1911[1], many new and exciting discoveries of superconducting materials have followed. Developments in the field of superconductivity have been motivated by the goal of reaching higher temperatures at which the onset of superconductivity can be observed. One area of material synthesis that has undergone significant growth in the past few decades is in the field of organic superconductors. Despite a number of advances, unanswered questions about organic superconductors remain and make them a very exciting and active area of study.

The field of organic superconductors has a long history. In 1964, W. A. Little published a paper predicting superconductivity in an organic material. He suggested that a conducting polymer with polarizable side chains could exhibit superconductivity at temperatures approaching, or even above, room temperature[2]. Although a superconductor with the mechanism Little suggested has not been realized, his paper stimulated further activity into synthesis of organic materials. After fifteen years of research in this area, the first organic superconductor was synthesized in 1979 when superconductivity was observed in pressurized bistetramethyl-tetraselenafulvalene-hexafluorophosphate ((TMTSF)$_2$PF$_6$)[3]. A number of organic superconductors were then realized by varying the anion (originally PF$_6$). Materials based upon TMTSF are now part of a broader category called the charge transfer salts, which contains a number of crystals made up of a variety of organic building blocks.

The charge transfer salts (CTS) are of particular interest because they exhibit
CHAPTER 1. INTRODUCTION

Figure 1.1: The structure of the bisethylenedithio-tetrathiafulvalene (ET) molecule.

a variety of phenomena across their phase diagram. They are made up of layers of an organic molecule with poorly conducting layers of anions interspaced between the planes. The crystal structure of the CTS makes their electrical conductivity highly anisotropic, leading to quasi-1D and quasi-2D electronic properties. This attribute makes these materials an excellent tool for investigating low dimensional physics. As well, by chemically altering the organic molecule or the anion, crystal properties can be varied and investigated. In this thesis, I will discuss organic superconductors that have crystal structures based on the bisethylenedithio-tetrathiafulvalene molecule (BEDT-TTF, or ET for short), as shown in Figure 1.1. The layered crystal structure of the organic superconductors based on this molecule leads to quasi-two-dimensional behaviour.

Chapter 2 provides an overview of superconductor theory. I will start from the phenomenological models of superconductivity and then proceed to summarize Bardeen–Cooper–Shrieffer (BCS) theory. The pairing of electrons into Cooper pairs at the superconducting phase transition is a key concept in this theory. A discussion of pairing mechanisms involved in the superconducting state will then follow, as this is particularly important to the work discussed in this thesis. Chapter 3 will then discuss conflicting data on the pairing involved in organic superconductors. It will show that the nature of the superconducting state has still not been conclusively settled.

Using cavity perturbation, I am able to relate a change in the resonance bandwidth and resonance frequency to the surface impedance. The ambiguity regarding
the pairing of the ET superconducting state makes experiments that probe surface impedance valuable, as I am able to characterize the temperature dependence of the penetration depth. This yields direct information about the pairing. The approach used to carry out the analysis of surface impedance data and relate it to conductivity will be discussed in Chapter 4. Experimental details such as factors to take into consideration and information on how the data is obtained will be presented in Chapter 5.

I will then present results of two types of ET superconductors in Chapter 6. In particular, the temperature dependence of the complex conductivity and the superfluid density will be shown. While the pairing mechanism is still an open question, the results are compatible with dirty $d$-wave pairing.
Chapter 2

Superconductivity

Three years after he first liquefied helium, Heike Kamerlingh Onnes observed a complete disappearance of electrical resistance in mercury at low temperatures[1]. Zero d.c. resistivity below a critical temperature, $T_c$, is now recognized as one of the hallmarks of superconductivity. It follows from the existence of zero resistivity that currents will flow without dissipation in a superconductor, as demonstrated through observations of persistent currents in superconducting rings. The other hallmark of superconductivity is the expulsion of a magnetic field from within the superconductor, as observed in 1933 by Meissner and Oschenfeld[4]. In addition to the expulsion of a magnetic field when in the superconducting state, a weak field that is applied to a superconducting material in its normal state will also be expelled as it is cooled below $T_c$. The superconducting state will also be destroyed at a large enough magnetic field, designated the critical magnetic field $H_c$. Thus, any theory developed to explain superconductivity must explain both perfect conductivity and near perfect diamagnetism in macroscopic samples.

A complete microscopic theory was not put forward to explain superconductivity until decades after these experimental observations. In 1957, Bardeen, Cooper and Schrieffer[5] formulated a successful theory involving pairs of electrons known as Cooper Pairs. Before then, a number of phenomenological models were put forward to explain the observed phenomenon. The field of superconductivity has continued to be very active and in 1986 new questions emerged when Bednorz and Müller discovered a new class of superconductors[6] with much higher critical temperatures. This
new class exhibits the same phenomena as conventional superconductors in general; however, the microscopic pairing mechanism between the electrons has still not been settled. The organics also present an area of active research with their own unresolved question about the pairing mechanism.

2.1 Phenomenological Models

Phenomenological models are very helpful in understanding the context for many measurements on superconducting materials. A good starting point for gaining physical intuition for electrodynamics in the superconducting state is the successful phenomenological model that F. London and H. London developed in 1935[7], which is derived below.

Following a derivation similar to that of Waldram[8], the supercurrent density can be written in the usual gauge invariant quantum mechanical form as

$$J_s = i\hbar \frac{e}{2m}(\Psi^\ast \nabla \Psi - \Psi \nabla \Psi^\ast) - \frac{2e^2}{m} \Psi \Psi^\ast A, \quad (2.1)$$

where $e$ is the fundamental charge, $\hbar$ is the reduced Planck constant, $m$ is electron mass, $A$ is the magnetic vector potential, and $\Psi$ is the superconducting wavefunction. The amplitude of the wavefunction is set to be a constant but the phase can vary spatially. Having a constant amplitude is a limitation of the theory that was eventually overcome by Ginzburg–Landau theory, which will be discussed later in this section. $\Psi$ can now be written as $\sqrt{n_s} e^{i\theta}$ in order to normalize the wavefunction so that $\Psi^\ast \Psi$ is the effective pair density of electrons ($n_s$). The concept of pairs was not originally part of the London theory; however it is now standard practice to write the wavefunction in this way. Using this expression for the wavefunction, Equation 2.1 becomes

$$J_s = -\frac{2n_s e^2}{m} \left( \frac{\hbar}{2e} \nabla \theta + A \right). \quad (2.2)$$

Expressions that describe the hallmarks of superconductivity, known as the London equations, can be arrived at after some manipulations of this equation. The first London equation can be found by taking the time derivative of Equation 2.2, which
results in the expression

\[ \frac{\partial J_s}{\partial t} = -\frac{2n_s e^2}{m} \left( \frac{\hbar}{2e} \frac{\partial \theta}{\partial t} + \frac{\partial A}{\partial t} \right). \]  

(2.3)

To simplify further, the time derivative of the phase is related to the local pair energy, or two times the chemical potential, which yields

\[ \hbar \frac{\partial \theta}{\partial t} = -2\mu. \]  

(2.4)

Equation 2.3 then becomes

\[ \frac{\partial J_s}{\partial t} = \frac{2n_s e^2}{m} \left( \frac{\nabla \mu}{e} - \frac{\partial A}{\partial t} \right). \]  

(2.5)

The expression in parentheses can be thought of as the effective electric field, \( E_{\text{eff}} \), since the gradient of the electrochemical potential determines the flow of electrons. (Recall \( E = -\nabla V - \frac{\partial A}{\partial t} \).) We can introduce the London parameter, \( \Lambda = m/2n_s e^2 \). Thus, the final form of the first London equation becomes

\[ \frac{\partial (\Lambda J_s)}{\partial t} = E_{\text{eff}}. \]  

(2.6)

This equation is an expression for perfect conductivity. An applied electric field will accelerate electrons. This describes a supercurrent that does not decay.

Taking the curl of Equation 2.2, and using the fact that the curl of a gradient is zero, we arrive at the second London equation

\[ \nabla \times (\Lambda J_s) = -B, \]  

(2.7)

where \( B \) is the magnetic induction, equal to the curl of the magnetic vector potential. This equation can be used to show that magnetic fields are screened within the bulk of the superconductor by supercurrents near the surface. To arrive at this conclusion, Ampère’s law, \( \nabla \times B = \mu_0 J_s \), can be used to replace \( J_s \). Here, \( \mu_0 \) is the permeability of free space. The vector identity \( \nabla \times (\nabla \times B) = \nabla (\nabla \cdot B) - \nabla^2 B \) and the fact that \( \nabla \cdot B = 0 \) can be used to reduce Equation 2.7 to

\[ \nabla^2 B = \frac{B}{\Lambda_L^2}, \]  

(2.8)
where \( \lambda_L = \sqrt{m/(2\mu_0 n_s e^2)} \) is known as the London penetration depth. This is in the form of a screening equation, describing an exponential decay of magnetic field with depth over a characteristic length scale \( \lambda_L \). Equation 2.8 consequently describes the property of perfect diamagnetism.

A second, very successful phenomenological model is the Ginzburg–Landau theory, developed in 1950[9]. Starting from Landau’s theory describing second-order phase transitions, the Ginzburg–Landau theory brings in the wavefunction \( \psi \) by introducing it as a complex and position-dependent order parameter. This theory focuses on the superconducting electrons, with their local density defined as

\[
n_s = |\psi(x)|^2.
\]

Ginzburg and Landau proposed an expression for the free energy as an expansion in powers of \( \psi \) and \( \nabla \psi \) with phenomenological constants \( \alpha \) and \( \beta \). They wrote the expression for the free-energy density, \( f \), in the form

\[
f = f_{n0} + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m^*} \left| \left( \frac{\hbar}{i} \nabla - \frac{e}{c} A \right) \psi \right|^2 + \frac{\hbar^2}{8\pi},
\]

where \( c \) is the speed of light, \( h \) is the flux density on a microscopic scale, and \( f_{n0} \) is the free-energy density in the normal state with no applied field. One of the major successes of this theory is that, since \( \psi \) is a function of position, it can handle a spatial variation of the density of superconducting electrons. This theory also identifies another characteristic length,

\[
\xi(T) = \frac{h}{\sqrt{2m^*|\alpha(T)|}},
\]

known as the coherence length. It characterizes the minimum scale over which spatial variations of the order parameter \( \psi \) can occur without significant energy cost. \( \psi \) from Ginzburg–Landau theory can be thought of as the wavefunction describing the motion of the centre-of-mass of the Cooper pairs, which will be discussed in the next section. In fact, Gor’kov[10] showed in 1958 that Ginzburg–Landau theory is a limiting form of Bardeen, Cooper, and Shrieffer’s microscopic theory near \( T_c \).

The Ginzburg–Landau parameter is then defined as the ratio of the two characteristic lengths that describe a superconductor

\[
\kappa = \frac{\lambda}{\xi}.
\]
Figure 2.1: Depiction of the variation of the strength of magnetic field, $B(x)$, and $\psi$ at the normal-superconducting interface for Type I (left) and Type II (right) superconductors.

Both $\xi(T)$ and $\lambda(T)$ diverge with $(T - T_c)^{-1/2}$, and so this is a temperature independent value. It classifies a superconducting material. Materials with $\kappa \ll 1$ are known as Type I superconductors. Most classic superconductors fall into this category. It can be shown that the surface energy, the difference in free energy between the normal state and the superconducting state, is positive, thus they stably expel magnetic flux from the interior of the sample. Materials with $\kappa \gg 1$ are known as Type II superconductors, and the surface energy between the normal and superconducting state is negative. This leads to a mixed state in these superconductors in which the normal and superconducting states subdivide into domains[11].

### 2.2 BCS Theory

The only microscopic theory of superconductivity that is currently fully accepted is the highly successful microscopic theory for phenomenon seen in conventional superconductors known as the Bardeen–Cooper–Shrieffer (BCS) theory[5]. The key
The concept underlying this theory is that electrons will form an energetically favourable bound state\cite{12} known as a Cooper pair in the superconducting phase. Any electrons that experience an attractive interaction will form these Cooper pairs below a critical temperature. In BCS theory, electrons of opposite momentum and spin close to the Fermi surface will experience a mutual attraction that is mediated by the coupling of the electrons to phonons in the crystal lattice. Each electron pair can be treated as a single boson. The Cooper pairs extend over a large area in space and thus there is strong spatial overlap. The result is a cooperative binding in which all of the Cooper pairs condense to a state of the same energy, like a Bose–Einstein condensate, leading to a macroscopic wave function. This energy state is lower than that of the filled Fermi sea.

The BCS wavefunction that was proposed for $T = 0$ can be written in the second-quantized form\cite{8}

$$|\text{BCS}\rangle = \prod_{k} (u_{k} + v_{k}c_{k\uparrow}^{\dagger}c_{-k\downarrow}^{\dagger})|0\rangle. \quad (2.13)$$

Here $c_{k\uparrow}^{\dagger}$ and $c_{-k\downarrow}^{\dagger}$ are creation operators and $|0\rangle$ is the vacuum state. The electrons are in $(−k \downarrow, k \uparrow)$ pairs in this state, where $k$ is the wavevector in momentum space and the arrows represent spin. $u_{k}$ and $v_{k}$ are complex parameters, and $u_{k}^{2}$ and $v_{k}^{2}$ are the probabilities that the pair state is empty and full, respectively. Their sum, $u_{k}^{2} + v_{k}^{2}$, is equal to one.

The condensation of electron pairs into a lower energy state leads to an energy gap, $\Delta$, near the Fermi surface, as it will cost some energy to break the Cooper pairs apart. The energy gap means that a minimum energy of $2\Delta$ is necessary to break up a Cooper pair, which manifests itself as a gap of $2\Delta$ in the density of states. It can be shown\cite{8} that the gap function depends on momentum and that at $T = 0$ it will satisfy the self-consistency equation

$$\Delta_{k} = - \sum_{k'} \frac{\Delta_{k'}}{2E_{k'}} V_{k'k} \quad (2.14)$$

for an interaction potential $V_{k'k}$, dependant upon momentum. $E_{k}$ is the quasiparticle excitation energy, which is always positive.

In conventional BCS theory, it is assumed that the effective potential which pairs the electrons is attractive and spatially uniform. This results in a gap energy that is

\textit{CHAPTER 2. SUPERCONDUCTIVITY}
finite in every direction. This gap function has no angular dependence, similar to the $s$-shell for the hydrogen atom. For these reasons, the pairing in conventional superconductors described by BCS theory is said to be $s$-wave. Due to the antisymmetric nature of fermions, and because the pair wavefunction is even in angular momentum space, the BCS state is made up of spin-singlet electron pairs.

### 2.3 Pairing Symmetry

While $s$-wave pairing describes the behaviour of conventional superconductors like aluminium and tin, materials like the organic superconductors cannot be explained by the original BCS theory. The conventional pairing of electrons in the original BCS theory results in an energy gap that is finite everywhere and has the full crystal symmetry. In contrast, other materials can be very anisotropic in their gap function and are known as unconventional superconductors.

Motivated by research on superfluidity in helium-3 [13], it can be shown that pairing is possible in higher angular momentum channels. If the potential is nonuniform then Equation 2.14 can have solutions in other angular momentum channels. Where the potential is repulsive, the gap will go to zero. This will lead to nodes on the Fermi surface where $\Delta_k$ is equal to zero. The pairing symmetry can then be lower than the symmetry of the crystal. This is of importance in the context of heavy fermions and high-$T_c$ superconductors.

Of interest in the context of this thesis is the difference between $s$-wave superconductivity and $d$-wave superconductivity. $s$-wave superconductivity has an isotropic energy function whereas $d$-wave superconductivity has an anisotropic energy function, which changes sign around the Fermi surface. $d$-wave superconductors are so-named because the gap function varies as $\Delta(\theta) \approx \Delta_0 \cos(2\theta)$ with gap nodes at $45^\circ \pm n \cdot 90^\circ$ around the two-dimensional Fermi surface, where $n$ is an integer. This four-fold rotational symmetry is similar to the $d$-orbital. At the gap nodes, the energy to produce quasiparticle excitations is zero.

The density of states varies for different pairing symmetries in BCS theory. This is because it is determined by the structure of the gap function $\Delta_k$ through the
Figure 2.2: The density of states is shown for (a) \( s \)-wave superconductivity and (b) \( d \)-wave superconductivity. \( E \) is the quasiparticle energy multiplied by \( \hbar \). The red dashed line in (b) is for the dirty \( d \)-wave case, which will be discussed in Section 2.4.

\[
N(E) = \text{Re} \left\langle \frac{E}{\sqrt{E^2 - \Delta^2}} \right\rangle_{\text{FS}}. \tag{2.15}
\]

Here, \( \langle \ldots \rangle \) is an average over the Fermi surface and \( E \) is the quasiparticle energy.

There are a number of experimental methods used to probe the symmetry of the pairing in superconductors. The density of states can be probed by investigating the temperature dependencies of the superfluid density or by physical properties such as the heat capacity. Measurements of the low temperature behaviour of thermodynamic variables can then be used to differentiate between \( s \)-wave and \( d \)-wave states. The isotropic order parameter with a finite gap at every point on the Fermi surface for \( s \)-wave superconductors results in an activated exponential temperature dependence\[8\], \( \exp(-\Delta_0/k_bT) \), of thermodynamic properties such as the heat capacity. Here, \( k_b \) is the Boltzmann constant and \( \Delta_0 \) is the magnitude of the energy gap.

In contrast to the gap in \( s \)-wave superconductors shown in Figure 2.2a, the density of states grows linearly for line nodes as seen in Figure 2.2b. This is because, for the \( d \)-wave superconductors, the gap nodes allow excitations at arbitrarily low energies.
CHAPTER 2. SUPERCONDUCTIVITY

The heat capacity will then have a quadratic temperature dependence.

A good probe of the density of states is the superfluid density, which is defined as $\rho_s(T) \equiv 1/\lambda^2(T)$. It is related to the density of states through the equation\[15\]

$$\frac{\lambda_0^2}{\lambda^2(T)} = 1 - 2 \int_0^\infty dE \left( -\frac{\partial f}{\partial E} \right) N(E) = \int_0^\infty dE \tanh \left( \frac{E}{2k_BT} \right) \frac{\partial N(E)}{\partial E},$$

where $\lambda_0$ is the pure, zero-temperature penetration depth and $f(E/T)$ is the Fermi function. The superfluid density for $s$-wave superconductors will not have significant temperature dependence at low temperatures — this is because the finite energy gap in all directions imposes a minimum excitation energy resulting in activated exponential temperature dependence. For materials in which $N(E)$ has a low energy power law form, $\rho_s(T)$ directly reflects the power law in $N(E)$, which can be seen by carrying out a Sommerfeld expansion. In the case of a $d$-wave superconductor, $N(E) \propto E$ and $\rho_s$ will vary linearly with temperature. This is shown in Figure 2.4.

2.4 Dirty $d$-Wave Pairing

The use of superfluid density measurements to probe pairing symmetry in superconductors can be complicated by the presence of disorder in a sample. Disorder breaks Cooper pairs. The main effect is that disorder gives the quasiparticle excitations a finite lifetime. The theory of disorder in unconventional superconductors has been developed by a number of authors\[16–20\]. To address impurities, the self-consistent $t$-matrix approximation (SCTMA) is used. Impurities are approximated as defects at a point, and they are assumed to cause scattering in the $s$-wave channel. Near the unitarity limit, where the impurity is close to binding a quasiparticle at the Fermi energy, the scattering leads to a resonance with the low energy quasiparticle states in the $d$-wave superconductors.

In this section and the next, the quasiparticle energy will temporarily be denoted $\omega$ instead of $E$ as this is the norm for theoretical work in this field. Elsewhere in the thesis, $\omega$ denotes the angular frequency of the microwaves. In this presence of disorder, $\omega$ is renormalized as follows\[18\]

$$\omega \rightarrow \tilde{\omega} = \omega + i\pi \Gamma - \frac{N(\omega)}{\epsilon^2 + N^2(\omega)}.$$
The impurity scattering strength is characterized by $c$, the cotangent of the scattering phase shift. It characterizes the strength of an interaction, with $c \gg 1$ representing weak scattering and $c \ll 1$ representing strong scattering. In this equation, $\Gamma = n_i n / (\pi^2 D(\epsilon_F))$, where $n$ is density of conduction electrons, $n_i$ is the concentration of impurities, and $D(\epsilon_F)$ is the density of states at the Fermi level. $N(\omega)$ is the quasiparticle density of states as described by Equation 2.15. For the $d$-wave state and for a simple, cylindrical Fermi surface, the density of states equation can be written

$$
N(\omega) = \text{Re} \left\{ \frac{\bar{\omega}}{\sqrt{\bar{\omega}^2 - \Delta_0^2 \cos(2\theta)^2}} \right\}_{\text{FS}} = \frac{2}{\pi} K \left( \frac{\Delta_0^2}{\bar{\omega}^2} \right),
$$

(2.18)

where $K(x)$ is the complete elliptical integral of the first kind and $\theta$ is the angle around the Fermi surface.

For arbitrary scattering, where $c$ can take any value, $\bar{\omega}$ can be calculated as the root of

$$
\bar{\omega} = \omega + i\pi \Gamma \frac{N(\bar{\omega})}{c^2 + N(\bar{\omega})^2}.
$$

(2.19)

This leads to a residual density of states in the dirty limit where there is none in clean $d$-wave superconductors (Figure 2.2). To see how this affects the temperature dependence of the superfluid density in the presence of disorder, Equation 2.16 is replaced by[14]

$$
\frac{\lambda_0^2}{\lambda^2(T)} = \int_0^\infty d\omega \tanh \left( \frac{\omega}{2k_b T} \right) \text{Re} \left\{ \frac{\Delta_k^2}{(\bar{\omega}^2 - \Delta_k^2)^{3/2}} \right\}_{\text{FS}}.
$$

(2.20)

The density of states term can be rewritten in terms of complete elliptical integrals of the first (K) and second (E) kind

$$
\left\{ \frac{\Delta_k^2}{(\bar{\omega}^2 - \Delta_k^2)^{3/2}} \right\}_{\text{FS}} = \frac{2}{\pi \bar{\omega}} \left[ K \left( \frac{\Delta_0^2}{\bar{\omega}^2} \right) + \frac{\bar{\omega}^2}{\Delta_0^2 - \bar{\omega}^2} E \left( \frac{\Delta_0^2}{\bar{\omega}^2} \right) \right].
$$

(2.21)

The effect of disorder can be seen in Figure 2.3 and Figure 2.4. At low temperatures, the superfluid density varies linearly with $T$ in the clean limit and quadratically with $T$ when disorder is present. This is shown in contrast to the $s$-wave superconductor. The $s$-wave superfluid density does not have a substantial temperature dependence at low temperatures.
Figure 2.3: Plot of the effect of disorder on (a) the imaginary part of the renormalized quasiparticle energy and (b) the density of states.

Figure 2.4: Superfluid density for (a) $s$-wave superconductivity and (b) $d$-wave superconductivity. The red dashed line in (b) is for the dirty $d$-wave case. Here, $c = 0$ and $\Gamma = 0.005$. 
Chapter 3

BEDT-TTF Based
Superconductors

The first organic superconductor based on the BEDT-TTF molecule (Figure 1.1) was ET$_4$(ReO$_4$)$_2$, which was synthesized in 1983[21]. Many other organic superconductors based on ET were synthesized after this, including one of the first ambient pressure organic superconductors, β-ET$_2$I$_3$[22]. The composition of the ET salts can be quite varied; however, the most common ET salts have the stable stoichiometry of 2:1 organic molecule to anion, ET$_2$X. The anion X is typically an inorganic molecule. Even with the composition ratio fixed, crystal structures vary widely. In this chapter I will discuss the structure of the ET superconductors, then review existing experimental data in order to further motivate the issues this thesis will be addressing. The two materials that were the focus of this work are κ-ET$_2$Cu[N(CN)$_2$]Br and κ-ET$_2$Cu(SCN)$_2$. The κ in front of the chemical formula refers to the packing motif of the ET molecules and will be discussed in Section 3.2.

3.1 A Two-Dimensional Playground

The charge transfer salts have many interesting properties which make them an ideal playground for condensed matter physicists. A number of physically interesting phases can be experimentally accessed using pressure and magnetic fields because of the relatively low value of the upper critical field and superconducting transition
Figure 3.1: Illustration of the hopping amplitude between dimers. The dimers are represented by the pairs of dark black lines, and the hopping processes whose amplitudes are $t$ and $t'$ are indicated by the lines. The green lines and labels b and c represent the crystallographic axes.

temperature. Pressures on the order of kilobars can be used to tune through different phases.

The ET superconductors form in crystals with alternating layers of electron acceptors, X, and electron donors, ET. Focusing on the $\kappa$-(ET)$_2$X superconductors, the organic molecules pair in dimers with each dimer giving up one electron. This dimerization leads to half filling of each organic layer. This results in a band structure that is quasi-2D, similar to layered cuprates. Details about the electronic structure of the ET superconductors will follow in Section 3.2.

Each dimer can be considered a ‘site’ in the lattice model\cite{23}. The amplitudes for hopping between dimers are given by $t$ and $t'$ as shown in Figure 3.1. Geometric frustration will occur if the hopping integrals are the same magnitude. The ratio $t'/t$ will define how close the system is to frustration.

Kanoda has proposed a conceptual phase diagram to relate the interplay of potential and kinetic energies\cite{24}. With the band filling at a fixed value of one half,
competition between the effective Coulomb repulsion between electrons on the same dimer, $U$, and the kinetic energy, parametrized by the width of the conduction band, $W$, plays a large role in determining the location of the superconductor on the phase diagram. Where $U$ dominates, the result will be a Mott Insulator. At low temperatures, this dominance of $U$ manifests as an antiferromagnetic insulator. Where $W$ (determined by the magnitudes of $t$ and $t'$) dominates, delocalization leads to superconductivity at low temperatures. At higher temperatures, a metallic phase appears. This is shown in Figure 3.2.

Clearly, changes in the intermolecular spacing can greatly affect the electronic properties of the crystal. The effects of changing the intermolecular spacing can be
Figure 3.3: Pressure-temperature phase diagram for $\kappa$-(ET)$_2$X compounds. The arrows indicate the effective ‘chemical’ pressure for the different anions, X, relative to ambient pressure $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl. $H_8$-Cl indicates X= $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl, $H_8$-NSC indicates $\kappa$-(ET)$_2$Cu(NSC)$_2$, and $H_8$-Br and $D_8$-Br indicate hydrogenated and deuterated $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br, respectively. From B. J. Powell[29]; used with permission.

seen by studying materials with a different anion or by applying pressure. Figure 3.3 shows where several of the $\kappa$-(ET)$_2$X materials fall on a pressure-temperature diagram. Solid lines indicate phase boundaries between the paramagnetic (PM), the superconducting (SC), and the antiferromagnetic insulating (AFI) states. Experimental data on these phase boundaries can be found in References [25–27] and are also compiled into a pressure-temperature diagram in Reference [28]. Different anions will also change the unit cell volumes of a crystal. The change in volume leads to a change in behaviour comparable to what is observed when the pressure changes. In this way, the effective ‘chemical’ pressure of a system can be considered.
3.2 Structure of ET Based Superconductors

Within the ET molecule, Figure 1.1, the \( s \) and \( p \) orbitals of the carbon and sulfur atoms overlap and hybridize. The result is a strong intramolecular bond that exists between the atomic species, known as a \( \sigma \) bond. This hybridization will also form a \( \pi \) orbital that is perpendicular to the molecular ring plane. Because their binding energy is much lower than those in the sigma bond, the \( \pi \)-electrons are delocalized.

In order to form a conducting molecular crystal, the organic molecules will transfer, or “donate”, an electron to the inorganic electron acceptor molecule. For the 2:1 stoichiometry, a pair of organic donor molecules gives up one electron to molecule X. This leads to an unpaired \( \pi \)-electron. The partially filled \( \pi \) orbitals of the molecular rings overlap in the crystal structure, resulting in the \( \pi \)-electron delocalizing over the entire crystal and leading to electronic conduction.

The ET molecules can have a high packing density due to the planar nature of the \( C_6S_8 \) centre, which leads to many possible variations on packing arrangements[30]. ET salts made with the same inorganic molecule (with the same chemical structure) can have a number of packing motifs. These motifs are labelled using Greek characters, and the most important are the \( \alpha \), \( \beta \), and \( \kappa \) phases. These are illustrated in Figure 3.4.

The crystal structures of \( \kappa \)-ET\(_2\)Cu[N(CN)\(_2\)]Br and \( \kappa \)-ET\(_2\)Cu(SCN) are shown in Figure 3.5. Some features of the \( \kappa \)-(ET)\(_2\)X superconductors crystal structures are listed in Table 3.1.

The kappa stacking motif involves orthogonal dimers made of pairs of interacting ET molecules. The overlap of the molecular \( \pi \) orbitals leads to overlap between
Table 3.1: Crystal data for various $\kappa$-(ET)$_2$X superconductors at room temperature. V is volume of the unit cell and z is the number of molecular units per unit cell. The crystallographic axis perpendicular to the conducting plane for each crystal is underlined. ‡ Indicates newer results with dimensionality and thermal fluctuations taken into account. (Data from [30].)

the dimers and also between adjacent orthogonal dimers. The overlap is so strong between the dimers, that they can be considered as one unit. This arrangement results in electrical two-dimensionality with high conductivity in the plane of the ET molecules. The insulating anion layer suppresses the molecular overlap in the interlayer direction.

In order to understand the electronic structure, some approximations must be considered. Using the Molecular Orbital method, linear combinations of the s and p atomic orbitals form $\pi$ molecular orbitals perpendicular to the molecule. The $\pi$-electrons are assumed to be free over the entire molecule. A tight binding calculation can be made using the Highest Occupied Molecular Orbit (HOMO) approximation and information from available structural data[31, p. 137].

Because the intramolecular orbital overlap is much stronger than the overlap between the organic molecules, the calculated electronic structure yields a strictly two-dimensional Fermi surface, as shown in Figure 3.6. There are closed hole pockets and an open corrugated electron sheet. The Fermi surfaces for the various $\kappa$-(ET)$_2$X systems are all very similar. For further discussion on the specifics of these calculations, see Reference [32].
Figure 3.5: Crystal structure of $\kappa$-ET$_2$Cu(SCN)$_2$ (left) and $\kappa$-ET$_2$Cu[N(CN)$_2$]Br (right). Note that the interlayer axes perpendicular to the conducting plane are the a-axis and b-axis, respectively.

Figure 3.6: Fermi surface of $\kappa$-ET$_2$Cu(SCN)$_2$. 
3.3 Existing Data on Pairing Symmetry

Despite over 30 years of research on the superconducting state of the charge transfer salts, the pairing symmetry has still not been conclusively identified. There have been a number of contradictory experimental results. A recent review of these conflicting results is documented in Reference [33]. Some results provide evidence for nodes such as those that exist in $d$-wave superconductivity; however, other groups have found evidence that the pairing is fully gapped $s$-wave superconductivity.

Measurements of the heat capacity temperature dependence have shown that it is exponentially vanishing at low temperatures[28, 34]. This implies that the energy gap does not have any nodes, suggesting $s$-wave superconductivity.

On the other hand, penetration depth measurements have been carried out with results that seem be inconsistent. Conventional superconductivity is implied by some penetration depth measurements[35, 36], shown in Figure 3.7a. Other penetration depth measurements[37–39], suggest unconventional superconductivity.

![Figure 3.7](image_url)

Figure 3.7: (a) Penetration depth data for $\kappa$-(ET)$_2$Cu(NSC)$_2$ that suggests $s$-wave superconductivity. Data taken from D. R. Harshman[35]; used with permission. (b) Penetration depth data of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br (a and b) and $\kappa$-(ET)$_2$Cu(NSC)$_2$ (c and d) showing unconventional superconductivity. From A. Carrington[40]; used with permission. Copyright 1990 by The American Physical Society.
The most reliable data are those of Carrington et al. They demonstrated that the penetration depth had a fractional power law temperature dependence, $\lambda(T) \propto T^{3/2}$[40], shown in Figure 3.7b. This result is peculiar because the power law behaviour cannot be explained adequately by any current theory. Although the interpretation of this data is not clear, it is important to note that it is not consistent with a fully gapped order parameter. Clearly, more experiments are needed in order to conclusively solve the pairing symmetry question.
Chapter 4

Superconductor Microwave Electrodynamics

Microwave spectroscopy is a very powerful tool for investigating superconductivity because the frequencies correspond to relevant energies in the system, such as the superconducting energy gap and the quasiparticle scattering rate. It is also valuable because although the d.c. resistivity goes to zero in the superconducting state, the a.c. impedance remains finite. This is due to the finite inertia of the Cooper pairs. Being able to measure the a.c. impedance allows useful information to be extracted on the superconducting ground state and its excitations.

4.1 Two-Fluid Model

At finite frequencies, the London electrodynamics of Section 2.1 need to be extended to take into account the presence of quasiparticle excitations. The simplest way to do this is to use a generalized two-fluid model. The two-fluid model yields valuable information on conductivity.

This model considers the contribution to the conductivity at finite frequencies from both the superfluid and the quasiparticle excitations. The quasiparticle excitations are considered as a “normal” fluid that conducts in parallel with the superfluid. The
conductivity then has resistive and reactive components and can be written as
\[ \sigma = \sigma_1 - i\sigma_2. \] (4.1)

The first London equation describes the contribution of the superfluid component to the conductivity. Transforming Equation 2.6 into the frequency domain results in the expression
\[ i\omega J_s(\omega) = \frac{n_s e^2}{m} E(\omega). \] (4.2)
Here, I am using the convention that \( J(t) = \Re\{J e^{i\omega t}\} \) for time-harmonic phasor fields. From this point forward, \( \omega \) will be used to denote angular frequency. Using Ohm’s law, \( J = \sigma E \), and the definition of \( \lambda_L \) in Equation 2.8, the contribution of the superfluid component to the conductivity can then be expressed as
\[ \sigma_{sf} = \frac{n_s e^2}{im\omega} = \frac{1}{i\omega\mu_0\lambda_L^2}. \] (4.3)

The conductivity due to quasiparticles can be approximated using the Drude model of electrical conductivity. The expression for \( \sigma_1 \) can be found by considering a scalar force equation for the normal charge carriers in the relaxation time approximation
\[ m\ddot{v} = \sum F = qE - \frac{mv}{\tau}, \] (4.4)
where \( \tau \) is the relaxation time of the quasiparticles, \( F \) stands for force, and \( v \) is velocity.

Rearranging Equation 4.4 and transforming the equation into the frequency domain yields
\[ v = \frac{qE}{m} \frac{1}{(i\omega + 1/\tau)}. \] (4.5)
Using the fact that \( J = n_n qv \), where \( n_n \) are normal electrons, and also \( J = \sigma E \), the final result for Drude conductivity is
\[ \sigma = \frac{n_n q^2}{m} \frac{1}{(i\omega + 1/\tau)}. \] (4.6)

From this result, replacing \( q \) with electron charge \( e \) in the final step, it can be seen that
\[ \sigma_1 = \frac{n_n e^2\tau}{m} \frac{1}{(\omega^2\tau^2 + 1)}. \] (4.7)
It is interesting to note that the contribution of the superfluid to the conductivity can be arrived at by taking the limit as $\tau$ goes to infinity; however, this is not the correct way to think about the superfluid. It has been properly treated in Section 2.1, where it emerges as a consequence of wavefunction rigidity.

Although it is convenient, the Drude model conductivity is only an approximate description. This is because it is well known that the relaxation rate for different electronic states is not the same in real materials. For the case of impurity scattering in a $d$-wave superconductor, Hirschfeld and co-workers have shown that to a good approximation, the simple Drude model is replaced by an energy-averaged form\[19\]

$$\sigma_{qp} \approx \frac{e^2}{m} \int_{-\infty}^{\infty} \left( -\frac{\partial f}{\partial E} \right) N(E) \left\langle \frac{1}{1/\tau(E) + i\omega} \right\rangle_{FS} dE, \quad (4.8)$$

where $1/\tau(E)$ is the energy-dependent relaxation rate and the angle brackets indicate a Fermi surface average. It is very closely related to the imaginary part of the renormalized quasiparticle energy, shown in Figure 2.3a.

Combining these concepts, the generalized two-fluid model for the complex conductivity is written\[8\]

$$\sigma(\omega) = \frac{ne^2}{m} \left[ \frac{f_s}{i\omega} + \frac{f_n}{1/\tau + i\omega} \right], \quad (4.9)$$

where $f_s$ is the superfluid fraction and $f_n$ is the normal fluid fraction. In the clean-limit, $f_n + f_s = 1$.

The two-fluid model may seem overly simplistic at first, with its picture of interpenetrating fluids of normal and superconducting electrons. However, it can be placed on a solid physical footing by considering the conductivity sum rule. This sum rule is based on the fact that the electrical conductivity is a causal response function — the current cannot respond to electric fields that have yet to be applied. Causality imposed tight constraints between real and imaginary parts of the conductivity. At a sufficiently high frequency, the conductivity is dominated by the inertial response of the charge carriers and becomes purely imaginary. This then leads to the conductivity sum rule

$$\frac{1}{\pi} \int_{0}^{\infty} \sigma_1(\omega)d\omega = \frac{ne^2}{2m}. \quad (4.10)$$

When applied to the system of electrons, this means the total area under the $\sigma_1(\omega)$
Figure 4.1: Illustration of the real part of the conductivity spectrum for a clean-limit superconductor, with the red arrow representing the zero–frequency delta function. The upper panel shows the typical Drude conductivity for a superconductor above the critical temperature. The lower panel shows the superconducting state.

spectrum must be constant. Figure 4.1 depicts $\sigma_1(\omega)$ for a Drude conductivity in the normal state.

Because there is no dissipation associated with the superfluid, it cannot contribute to the real part of the conductivity at any finite frequency. Instead, there is a superfluid delta function in $\sigma_1$ at zero frequency. The result can be derived using a Kramers–Krönig transform of the superfluid conductivity, Equation 4.3, and leads to

$$\sigma_{1, sf} = \pi \frac{n_s e^2}{m} \delta(\omega),$$  

(4.11)

which clearly only contributes to the conductivity at zero–frequency, as anticipated. Another way to think of this is that it represents the energy absorbed when the superfluid is initially accelerated. The delta function from the superfluid contribution is required by Equation 4.10 and is depicted in the lower panel of Figure 4.1.
CHAPTER 4. SUPERCONDUCTOR MICROWAVE ELECTRODYNAMICS

4.2 Microwave Surface Impedance

Surface impedance is defined as the ratio of the tangential components of the electric and magnetic fields, \( E \) and \( H \), at the surface of the sample. It is a complex quantity defined as \( Z_s = R_s + iX_s \), where the surface resistance \( R_s \) is related to the power absorbed and the surface reactance \( X_s \) is related to the inductive response. In the local electrodynamic limit, where the penetration depth is much larger than the coherence length and quasiparticle mean free path (this restricts us to type II superconductors), we can write \( J(r) = \sigma E(r) \). This allows a simple solution of the field penetration problem at a conducting surface leading to the following relation between surface impedance and complex conductivity

\[
\sigma = \frac{i\omega\mu_0}{Z_s^2},
\]

(4.12)

where \( \omega \) is the angular frequency at which the measurement is taken.

In the normal state, the conductivity will be dominated by the real component \( (\sigma_1 \gg \sigma_2, \text{ or } \omega\tau \ll 1) \). The real and imaginary components of the surface impedance are then approximately equal

\[
R_s \approx X_s \approx \sqrt{\omega\mu_0\rho/2},
\]

(4.13)

where \( \rho \) is the d.c. resistivity. Knowing that \( R_s \) and \( X_s \) should be equal in the normal state allows the absolute value of \( X_s \) (otherwise unmeasurable by us) to be determined by matching \( R_s \) and \( X_s \) above \( T_c \).

In the superconducting state the superfluid response is much larger than the dissipative response, making \( \sigma_2 \gg \sigma_1 \). The surface reactance is then approximately

\[
X_s(\omega, T) \approx \mu_0\omega\lambda(T),
\]

(4.14)

where \( \lambda(T) \) is the penetration depth. In the superconducting state, the surface resistance also has a convenient expression in this limit,

\[
R_s(\omega, T) \approx \frac{1}{2} \omega^2 \mu_0^2 \lambda^3 \sigma_1.
\]

(4.15)
Figure 4.2: (a) Depiction of the resonator and sample geometry. The coupling loops inductively couple energy into and out of the resonator and are fixed in place at the beginning of the experiment. From P. Carrière [41]; used with permission. (b) Depiction of a cross-section of the resonator illustrating the microwave magnetic field in the base mode. The volume of the cavity is approximately 1 cm$^3$. The red field lines in (b) illustrate the magnetic field for the TE011 mode. The field is shown for one half of the resonator. From W. A. Huttema[42]; used with permission.

4.3 Cavity Perturbation

To probe the microwave electrodynamics of a superconductor, we perform cavity perturbation measurements on the sample. We use a dielectric resonator in a superconducting cavity in order to couple the microwaves and the sample. The resonator also amplifies the electromagnetic interaction between the signal and the sample. The cylindrical geometry is shown in Figure 4.2a. In this way, the surface impedance of low loss samples like superconductors is measured as the experimentally accessible quantity. By choosing particular microwave modes, we set up well defined fields around the sample, with the local magnetic fields being approximately uniform and with a node in the electric field at the sample’s location (Figure 4.2b). From this, information about the conductivity is calculated as discussed in Section 4.1.

Cavity perturbation allows us to obtain measurements of the surface impedance through a direct relationship to changes in the center frequency, $f_0$, and the bandwidth, $f_b$, of the resonator. The method to relate these quantities is based on the
work of Huttema et al.\cite{43}, who followed the methods of Altshuler\cite{44} and Ormeno et al.\cite{45}.

The general cavity perturbation result is
\[
\Delta f_0 + \frac{i \Delta f_b}{2} \approx \left\{ \frac{i}{2\pi} \int_S \Delta Z_s \tilde{H} \cdot \tilde{H}' dS - f_0 \int_V \left[ \Delta \mu \tilde{H} \cdot \tilde{H}' + \Delta \epsilon \tilde{E} \cdot \tilde{E}' \right] dV \right\} / 4U,
\]
where $\Delta f_0$ is the perturbative shift in the resonance frequency and $\Delta f_b$ is the perturbative shift in the half-power bandwidth. Further details about these two quantities will be discussed below. Here, $U$ is the electromagnetic energy stored in the resonator, $\tilde{H}$ and $\tilde{E}$ indicate the complex phasor fields, $\Delta \epsilon$ is the change in permittivity, and $\Delta \mu$ is the change in permeability. The unprimed fields are the fields for the empty-resonator, and the primed fields represent the perturbed fields when a sample is introduced. $S$ and $V$ are the surface area and volume of the resonator, respectively. In microwave cavity perturbation, the superconducting sample is treated as the inside surface of the resonator.

For my measurements, I take measurements at various temperatures, and it is the change in temperature of the sample causes the measured perturbation. The volume integral can be ignored because the permeability and permittivity are not changing. The final result is
\[
R_s(T) + i \Delta X_s \approx \Gamma \left\{ \frac{\Delta f_b(T)}{2} - i \Delta f_0(T) \right\}
\]
where $\Gamma = 8\pi U / \int_S \tilde{H} \cdot \tilde{H}' dS$ and is constant for a given sample and resonator mode. $\Delta f_b(T)$ is the shift in bandwidth with respect to the empty resonator. $\Delta f_0(T)$ is the difference in resonant frequency from that measured at a reference temperature.

The sample is mounted on a silicon rod and this will contribute to values of $\Delta f_0$. These are taken into account by taking a baseline measurement with no sample on the rod. This is shown in Section 5.1. All of the measurements in this thesis were taken at the base mode of 2.91 GHz.

By directly measuring $R_s$ and $X_s$ with cavity perturbation, information on the conductivity can be determined. In particular, relating $\sigma$ to $Z_s$ allows the superfluid density ($\rho_s \equiv 1/\lambda^2$) to be investigated through the relationship in Equation 4.3.
Chapter 5

Experimental Considerations

A number of experimental considerations were necessary during my investigation of superconducting organic materials. In this chapter, I will describe them.

5.1 Sample Puck

At the start of this project, a new mounting structure was fabricated. This was necessary in order to measure the in-plane response of the highly electrically anisotropic organic superconductors. The new mounting structure, called a sample puck, allows the crystal to be measured in a different orientation from that used in previous measurements. The sample mounting orientations are illustrated in Figure 5.1. The different mounting orientation allows surface currents to be set up along different crystallographic axes. For the organic samples, currents are set up along the highly conductive plane when mounted on this new puck. This is because in this new orientation, the magnetic field is perpendicular to this plane.

The sample is mounted on a silicon rod using a small quantity of vacuum grease. This rod acts as a ‘hot finger’ that allows the sample to be heated independently from the resonator. The resonator is then kept at a fixed temperature. This allows the measured perturbations of the resonant frequency and bandwidth to be limited to changes in the sample and not the resonator.

Silicon was chosen for the hot finger because it has high thermal conductivity and because its dielectric absorption is small at low temperatures. (The low temperature
Figure 5.1: Depiction of the orientation of a sample for (a) the previous puck compared to (b) the new puck. The blue arrows represent the local magnetic field near the sample. From P. Carrière[41]; used with permission.

loss tangent of silicon is not well known, but we estimate that in the ultra high purity material we use it is less than $10^{-5}$. In any case, our background measurements on a bare silicon rod indicate that its microwave absorption is insignificant.)

Figure 5.2 shows the measured contribution of the silicon rod to the frequency shift. A fit to the resonant frequency as a function of temperature was carried out in Mathematica, so that the temperature dependent signal could be determined and used as a correction to subsequent experiments. At low temperatures, where the sample is in the superconducting state, the contribution to the microwave signal is very small. Its contribution is on the order of 10 Hz compared to the sample signal of $10^4$ Hz.
Figure 5.2: Contribution to the resonant frequency shift of the microwave signal from the silicon rod.

5.2 Thermometry

A new heater and resistive temperature sensor had to be mounted onto the new puck in order to measure and control the temperature of the sample. Ruthenium oxide resistors, RuO$_2$, were used for this purpose. This required calibration of the resistive sensor by recording the resistance of the uncalibrated sensor while measuring temperatures with a known calibrated sensor.

The first step is to convert the values of resistance using the equation

$$X = \frac{(2 \log R - (\text{max} + \text{min}))}{(\text{max} - \text{min})},$$

where $R$ is the resistance in ohms, $\text{max} = \text{Max}[\log R]$, $\text{min} = \text{Min}[\log R]$, and $X$ is a normalized variable. The known temperature is then plotted versus the $X$ values, as shown in Figure 5.3.

For typical low temperature sensors, the temperature dependent resistance is parametrized by a polynomial curve fit based on Chebyshev polynomials. Once resistances are converted to values of $X$, a polynomial equation is fit to the data. The
Figure 5.3: Plot of temperature versus resistance converted to X values. A polynomial equation based on Chebyshev polynomials is fit to the data.

Figure 5.4: Calibration curve for the new temperature sensor.
polynomial equation used is

\[ T(X) = \sum a_n t_n(X), \]  

(5.2)

where \( T(x) \) represents the temperature in Kelvin, \( t_n(X) \) is a Chebyshev polynomial, and \( a_n \) is the coefficient of the Chebyshev polynomial. The sum goes from zero to the order of the fit, \( n \). Chebyshev polynomials are defined by the relation

\[ t_n(X) = \cos[n \cdot \arccos(X)]. \]  

(5.3)

The X values can then be converted back to resistances. This results in a calibration curve for the new temperature sensor as shown in Figure 5.4.

### 5.3 Sample Preparation

The experiments on pairing symmetry would not be possible without the synthesis of high quality crystals. The search for higher \( T_c \) systems therefore involves strong collaborations between condensed matter physicists and chemists in the field of organic superconductors. The charge transfer salts are grown with a redox reaction using the electrocrystallization technique[31] illustrated in Figure 5.5a. The donor ET molecules are placed in an anode compartment and a supporting electrolyte is added to the cathode compartment. Platinum electrodes are used, and a constant current power supply is connected to the electrodes[46].

The samples investigated in this thesis were grown by the Powell group at the University of Queensland using this electrocrystallization technique. Most of the crystal samples were influenced by the use of a platinum wire as the growing site. This wire has a curvature and as a consequence one side of the crystals tend to mirror this curvature (Figure 5.5b). The sample was mounted so that the affected side was facing outwards in order to have a flat mounting surface.

For the experiments that I conducted for this thesis, the samples were cooled slowly (between 0.5 and 1.5 K/min) when placed into the experimental apparatus. This minimizes the possibility of freezing in intrinsic disorder because cooling the sample slowly eliminates the risk of the anions between the conducting layers freezing into disordered orientations.
Figure 5.5: (a) An example of a cell used for electrocrystallization. (b) Photo of $\kappa$-(ET)$_2$Cu(NSC)$_2$ sample. The rod the sample is mounted on is 1 mm by 1 mm. Note the curvature caused by the growth process.

Figure 5.6: Illustration of the possible endgroup orientations for ET molecule. The view along the molecule’s long axis is shown on the right.
Another reason to cool slowly is to reduce the disorder associated with the orientation of the ethylene end-groups. When forming a crystal, the ET molecule becomes planar at the center. The outer carbon-carbon bonds are non-planar and the ethylene endgroups can have two different relative orientations, staggered or eclipsed, as shown in Figure 5.6. At higher temperatures, the orientation will be disordered. At low temperatures, the end-groups will adopt a fixed orientation that depends upon the crystal structure and the inorganic molecule. Cooling slowly in the vicinity of the ordering temperature results in the highest degree of end-group order. For ET based CTS, this temperature seems to be in the range of 70-90 K\(^{[30]}\).

### 5.4 Dilution Refrigerator

In order to investigate superconductors, it is important to perform measurements across a wide range of temperatures. In order to reach low temperatures, well below the boiling point of liquid helium, a dilution refrigerator is required. Using this technology, I was able to obtain data at temperatures as low as 0.1 Kelvin.

A dilution fridge is able to reach low temperatures using a mixture of \(^3\)He and \(^4\)He. The mixture is kept in the mixing chamber. When the mixture is cooled below 870 mK, there is a phase separation into a \(^3\)He-rich and a \(^3\)He-poor phase. As it is cooled further, the rich phase will become pure \(^3\)He and the poor phase will approach a constant concentration of 6.6\% \(^3\)He. Moving \(^3\)He from the pure phase to the dilute phase provides cooling power through the endothermic latent heat of the phase transition.

In order to maintain a continuous cycle, a pump is used on the dilute \(^3\)He. This is possible because the vapour pressure of \(^3\)He is much higher than that of \(^4\)He at low temperatures. By pumping on the dilute \(^3\)He phase, more \(^3\)He will flow from the concentrated phase across the phase boundary. A continuous cycle is established by recondensing the \(^3\)He vapour and injecting it back into the concentrated phase. This cycle is shown in a simple schematic in Figure 5.7. More details can be found in Reference \(^{[47]}\).

Another useful property of the dilution fridge is that it has distributed cooling power at different temperatures. This is done using a series of cooling stages along
the fridge. By carefully ensuring thermal anchoring and thermal isolation between various components, low temperatures can be achieved.

A 1 K pot near the top of the fridge works as a heat sink for the circulating $^3$He. We take advantage of this by thermally anchoring the resonator to the 1 K pot and holding it at a temperature close to 1 K. The resonator temperature can be regulated to $\sim$1 mK. The sample stage is thermally anchored to the mixing chamber. A weak thermal link is used so that the temperature of the sample can be tuned over a wide range.

One challenge in microwave cavity perturbation measurements is that the sample and resonator must be mounted rigidly with respect to one another and be in close physical proximity while avoiding an unacceptable heat leak between the sample stage and the resonator. In order to accomplish this, the heat flow is intercepted at intermediate temperatures and diverted into the heat exchanger. The heat exchanger sits at about 300 mK and has spare cooling capacity. The temperature gradients are illustrated in Figure 5.8.

Figure 5.7: Simplified schematic of a $^3$He-$^4$He Dilution Refrigerator.
Figure 5.8: Colour coded image to illustrate the temperature profile in the experiment. From P. Carrière[41]; used with permission.
Chapter 6

Analysis and Results

Single crystals of ET$_2$Cu[N(CN)$_2$]Br and ET$_2$Cu(SCN)$_2$ were the two organic superconductor samples investigated. This was done using the cavity perturbation technique described in Section 4.3. A vector network analyser (VNA) acts as a source and detector for the microwave signal. The signal transmitted through the resonator is detected, and both the phase and the amplitude of the transmitted signal can be obtained. Background contributions from paramagnetic impurities in the dielectric resonator are reduced in our experiment by ensuring the output power of the resonator is kept constant as the temperature of the sample is changed. Values for the resonant bandwidth and centre frequency are extracted using a LabVIEW fitting routine that fits to the measured complex transmission amplitude to the sum of complex Lorentzian and direct coupling amplitudes, and are output into a file for analysis. Further details can be found in Reference [43].

The temperature of the organic sample was set using a temperature controlled stage located outside the resonator and thermally linked to the sample via the silicon rod ‘hot finger’ as discussed in Section 5.1. Figure 6.1 is an example of typical raw data from these measurements. In this chapter, I will show how this data is analysed in order to interpret the electronic behaviour of the superconducting samples.
6.1 Surface Impedance and Complex Conductivity

All of the measurements were taken at the resonator’s fundamental resonant frequency of 2.91 GHz. This is the most stable mode of the resonator. Values for $\Delta f_0$ and $\Delta f_b$ were recorded at fixed temperatures, from 0.1 K to 30 K. A reference temperature was chosen for each sample, and this reference temperature was periodically returned to throughout the experiment. This is done in order to record temperature drift, which occurs during long duration measurements done over several days. The drift can then be taken into account in order to adjust the data accordingly.

In addition to drift correction, the background $\Delta f_b$ for an empty resonator was subtracted from the signal to adjust the surface resistance data. The data were also corrected for the silicon rod contribution, as described in Section 5.1, although this correction is negligible below 10 K.

From the adjusted values for $\Delta f_0$ and $\Delta f_b$, $R_s$ and $X_s$ were calculated using the cavity perturbation approximation (Equation 4.17). The resonator constant, $\Gamma$, was
then determined for each given sample. Recognizing $\Gamma = \frac{2R_s}{\Delta f_b}$ by definition, this expression is then substituted into the equation for $R_s$ in the normal state, Equation 4.13. The final expression to calculate $\Gamma$ is

$$\Gamma = \frac{\sqrt{\omega \mu_0 \rho_{dc}}}{\Delta f_b}.$$  \hspace{1cm} (6.1)

In order to calculate $\Gamma$ for my samples, I used literature values of $\rho_{dc}$\cite{48} and experimental values for $\Delta f_b$, both at 30 K. This scale factor is one of the largest sources of error, and is accurate within 5-10%.

In the initial analysis, all power absorption by the sample was attributed to its surface resistance and this yielded an unphysically large surface resistance. This, combined with a tendency in some samples for the apparent surface resistance to show strong power dependence, indicated that there were extrinsic loss mechanisms acting in addition to the intrinsic electromagnetic absorption of the quasiparticle excitations. This is most likely due to extended defects in the sample. Therefore, the values of $R_s$ were shifted by making the assumption that surface resistance goes to zero at zero temperature. The remainder of the data presented were all shifted using this assumption by subtracting the minimum value of $R_s$ from each $R_s$ value.

The temperature dependence of $R_s$ and $X_s$ should be the same above $T_c$, as discussed briefly in Section 4.2. This is because $\omega \tau \ll 1$ and so the conductivity is purely real in the normal state. The result is that $R_s$ and $X_s$ are equal above $T_c$. Building on this concept, the values for $\Delta X_s$ are offset by a constant so that the values of $X_s$ match that of $R_s$ in the normal state to set the absolute value of the sample reactance.

Contrary to these expectations, in our earlier measurements it was found that the temperature slopes of the surface reactance and surface resistance did not match in the normal state. This discrepancy in the slope leads to a deviation between the surface reactance and surface resistance at temperatures above the critical temperature. This deviation can be seen in Figure 6.2a. The geometry of the earlier samples may have been causing the normal state divergence. The samples were generally triangular in shape, with sharp corners. Our suspicion is that the surface currents in the superconductors were travelling in the interlayer direction at the corners. Choosing different samples that were more hexagonal in shape led to a better matching of $R_s$. 
Figure 6.2: Matching the surface reactance to the resistance for ET$_2$Cu[N(CN)$_2$]Br. (a) Divergence of the normal state surface resistance and reactance, presumably due to surface currents flowing in the interlayer direction. (b) The divergence has been eliminated by choosing a sample without sharp corners, such as that pictured in Figure 5.5b.

and $X_s$, as shown in Figure 6.2b.

The complex conductivity, $\sigma = \sigma_1 - i\sigma_2$, was then obtained using Equation 4.12. The results of this analysis are shown in Figure 6.3. The plot range was reduced in order to focus on the real part of the conductivity in Figure 6.4.

### 6.2 Superfluid Density

Recall the superfluid density, $\rho_s$, is defined as

$$\rho_s(T) \equiv 1/\lambda^2(T) \approx \omega\mu_0\sigma_2(T).$$

(6.2)

Upon examination of Equation 4.3 the second relation is clear. Thus, the the imaginary part of the complex conductivity yields information about the superfluid den-
Figure 6.3: Complex conductivity of (a) ET$_2$Cu[N(CN)$_2$]Br and (b) ET$_2$Cu(SCN)$_2$.

Figure 6.4: Expanded image of the real part of the complex conductivity for (a) ET$_2$Cu[N(CN)$_2$]Br and (b) ET$_2$Cu(SCN)$_2$. 
Figure 6.5 shows the superfluid density for the two organic superconductors investigated. Qualitatively, both samples appear to exhibit a linear temperature dependence across a wide range of intermediate temperatures. This was shown in Section 2.4 to be expected for a $d$-wave superconductor. At low temperatures, the temperature dependence of the superfluid density appears to cross over to power law behaviour with an exponent close to two.

In light of the results of Carrington et al.[40], who report an unusual $T^{1.5}$ power law (Figure 3.7b), we plot our superfluid density data versus $T^{1.5}$ in Figure 6.6. Surprisingly, given that fractional power laws are not predicted in fermionic theories of superfluid density, we get a good correspondence: the superfluid density appears linear over a large range when plotted against $T^{1.5}$. However, it is important to test
the robustness of this sort of visualization in revealing the correct asymptotic power law at low temperature.

**Figure 6.6** illustrates a plot of a purely linear-to-quadratic crossover function based on the expression \( \rho_s(T) = 1 - \left( \frac{T}{T^*} \right)^2 \), motivated by Hirschfeld\[17\]. Here, \( T^* \) is the crossover temperature between linear and quadratic behaviour. This function is then plotted versus \( T^2 \) and \( T^{1.5} \). Interestingly, the best fit appears to be to \( T^{1.5} \), except at the very lowest temperatures. This is despite the fact that the function describes a pure crossover from \( T \) to \( T^2 \). This illustration emphasizes the importance of taking data to the lowest temperatures possible. It is only in this limit that the true asymptotic behaviour is revealed.

The temperature dependence of the experimentally determined superfluid density was then investigated by fitting the data to a similar crossover function

\[
\frac{1}{\lambda^2(T)} = \frac{1}{\lambda^2(0)} - \frac{aT^2}{T + T^*},
\]

The results of this fit are summarized in Table 6.1 and shown in Figure 6.5. Although
Figure 6.7: (a) Plot of \( \rho_s(T) = 1 - \frac{(T/T^*)^2}{((T/T^*) + 1)} \) as a function of \( T \). (b) The same function plotted versus \( T^2 \). Note the linear regime is not immediately apparent. (c) Low temperature portion of the curve shown in (b). In order to really see the quadratic behaviour it is necessary to go to very low temperatures. (d) The crossover function versus \( T^{1.5} \). Note the function appears very linear except at low temperatures. This gives the false impression that the asymptotic low temperature power law is \( T^{1.5} \), whereas the curve is simply crossing over from one integer power law to another.
Figure 6.8: Low temperature zoom in of superfluid density for (a) ET₂Cu[N(CN)₂]Br and (b) ET₂Cu(SCN)₂ from Figure 6.5. Note the quadratic temperature dependence at low temperatures.

The error in \( \frac{1}{\lambda^2(0)} \) is given based on the 95% confidence interval, the actual error will be much larger due to uncertainties in the scale factor as discussed in Section 6.1. It was found that \( \lambda(0) \) is 3.6 \( \mu m \) and 1.05 \( \mu m \) for the ET₂Cu[N(CN)₂]Br and ET₂Cu(SCN)₂ samples, respectively. It is difficult to compare the calculated \( \lambda(0) \) with literature values as exact values are still not agreed upon due to the strong anisotropy in organic samples; however, the values are thought to be on the order of 1-2 \( \mu m \)\cite{40}.

The crossover from linear to quadratic temperature dependence in the experimen-

<table>
<thead>
<tr>
<th>( \kappa )-ET₂Cu[N(CN)₂]Br</th>
<th>( \frac{1}{\lambda^2(0)}(\mu m^{-2}) )</th>
<th>( a (K^{-1} \mu m^{-2}) )</th>
<th>( T^*(K) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \kappa )-ET₂Cu[SCN]₂</td>
<td>0.904±0.001</td>
<td>0.16±0.02</td>
<td>3.3±0.6</td>
</tr>
<tr>
<td>( \kappa )-ET₂Cu[SCN]₂</td>
<td>0.0762±0.0001</td>
<td>0.0095±0.0003</td>
<td>2.8±0.3</td>
</tr>
</tbody>
</table>

Table 6.1: Fit parameters for the superfluid density fit to Equation 6.3. The error in these parameters is calculated by taking the difference between the parameter value and the endpoint of the 95% confidence interval.
tal $\rho_s(T)$ suggests that strong-scattering defects are present in the samples\cite{17}. This result strongly indicates that disorder is relevant in this system and is consistent with theories for strong-scattering in $d$-wave superconductors. This behaviour was illustrated in Figure 2.4b for the SCTMA theory of dirty $d$-wave superconductors. The crossover to a quadratic temperature dependence is demonstrated most clearly in Figure 6.8 and it is accurately quadratic below 0.8 K and 1.2 K for ET$_2$Cu[N(CN)$_2$]Br and ET$_2$Cu(SCN)$_2$, respectively.
Using microwave cavity perturbation, surface impedance measurements were carried out on two organic superconductor samples. My measurements on the superconductors $\kappa$-ET$_2$Cu[N(CN)$_2$]Br and $\kappa$-ET$_2$Cu(SCN)$_2$ provide a clear picture of the symmetry of the electron pairs in the superconducting state of these crystals.

The organics have a very rich phase diagram, as discussed in Chapter 3. Organic crystal samples are very also interesting because decades after first being synthesized, the pairing symmetry is still not agreed upon.

Using microwave cavity perturbation technique, described in Chapter 4, I was able to experimentally determine surface impedance as a function of temperature for the crystals measured. A number of experimental considerations were necessary, and in Chapter 5 these were discussed. I fabricated a new sample puck that allowed me to measure the in-plane response of the highly electrically anisotropic organic superconductors at the 2.91 GHz base mode of the resonator. The shape of the samples was an important consideration, and the electrocrystallization growth method was discussed in order to explain the curvature of the sample faces.

Finally, in Chapter 6 I showed my results of superfluid density analysis with respect to pairing symmetry that was first discussed in Chapter 2. Analysis of the surface impedance data showed a linear temperature dependence at intermediate temperatures and a crossover to a higher power law at low temperatures. These surface impedance measurements are congruent with $d$-wave superconductors with defects. These results challenge existing data on the pairing symmetry involved in...
the organic superconductors.

Future work should include further measurements on samples with differing geometry. Surface currents flowing in the interlayer direction due to sharp corners and potential extended defects are issues that were identified in the crystals used for this thesis. Sample selection is very important because getting reliable data is contingent on the crystal quality.
Bibliography


