Precision Measurements of Magnetic Penetration Depth in YBa$_2$Cu$_3$O$_{7-\delta}$

by

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Abstract

Using sensitive cavity perturbation techniques, we have performed extensive measurements of the microwave surface impedance of high quality single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. We have employed a novel loop-gap resonator with operating frequency at about 1 GHz and quality factor of $1 \times 10^6$ to $4 \times 10^6$ to probe the electrodynamics of the superconducting state of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The main focus of the thesis has been on the precision measurements of the magnetic penetration depth. We have studied the superconducting region of the phase diagram of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by measuring single crystals with various amounts of oxygen doping, ranging from underdoped ortho-II phase ($\delta = 0.5$) to the fully oxygenated ($\delta = 0$; slightly overdoped). The role of impurities have been studied by introducing controlled amounts of Zn, Ni, and Ca impurities into the crystals. A new generation of ultra high purity single crystals were grown at UBC using $\text{BaZrO}_3$ crucibles. Observation of extremely long quasiparticle scattering times in these higher purity crystals opened a new chapter in microwave spectroscopy of quasiparticles in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at our laboratory. Measurements of magnetic penetration depth performed in this thesis have been a continuous contributing factor to these studies. Also careful measurements of magnetic penetration depth near the transition temperature $T_c$ has revealed non-mean field behaviour consistent with 3D-XY critical fluctuations.
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Preface

The author has included previously published material as part of this thesis in Chapter 3. Full details of these publications are given below:


The 3rd and 4th publications which contain measurements of magnetic penetration depth and surface resistance at 1 GHz, concerns experimental work done entirely by myself during the course of my Ph.D. program.
In 1st and 2nd publications, the data is constructed from two independent types of experiments, the magnetic penetration depth, in the three crystallographic directions, \( \hat{a}, \hat{b}, \hat{c} \) and the surface resistance measured in the same directions. All of the magnetic penetration depth data was obtained as part of my thesis project.

In the last publication, the penetration depth data required to construct all of the microwave conductivity results were obtained by myself. In addition, I provided surface resistance measurements for one of the fine frequencies reported in the paper. This was in fact the first time that surface resistance measurements were obtained at a frequency as low as 1 GHZ.

Signature of the research supervisor;
Chapter 1

Introduction

1.1 Local Electrodynamics of Metals and Superconductors

In this section, we present a phenomenological approach towards the response of a conductor to electromagnetic radiation. Maxwell’s equation are obviously the starting point and after a simple algebra, one can derive the wave equation

\[-\nabla^2 \vec{H} = \vec{\nabla} \times \vec{J} - \epsilon \mu_0 \frac{\partial^2 \vec{H}}{\partial t^2}\]  \hspace{1cm} (1.1)

where \(\vec{H} = \vec{H}(\omega, t)\) is the applied magnetic field and \(\vec{J} = \vec{J}(\omega, t)\) is the induced current density in the conductor. A knowledge of the relationship between the current density and the applied fields is required in order to solve the above equation. Here, we distinguish two different cases, a normal metal and a superconductor.

Case of a Metal

For a normal metal in the local limit, Ohm’s law describes the current-field relationship.

\[\vec{J}(\omega, t) = \sigma(\omega) \vec{E}(\omega, t)\]

where \(\vec{E}\) is the applied electric field. Replacing \(\vec{J}\) in eqn. 1.1 and taking \(\mu = \mu_0\) leads to

\[-\nabla^2 \vec{H} = -\mu_0 \sigma \frac{\partial \vec{H}}{\partial t} - \epsilon \mu_0 \frac{\partial^2 \vec{H}}{\partial t^2}\]  \hspace{1cm} (1.2)

The solution to this equation gives propagating fields within the conductor with the propagation constant \(\kappa\),
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At low frequencies, the second term (due to displacement currents) is very small, furthermore the conductivity \( \sigma \) is real and is simply the reciprocal of DC resistivity. In this case the propagation constant reduces to

\[
\kappa^2 = \frac{1}{\delta^2}, \quad \delta = \sqrt{\frac{2}{\omega \mu \sigma}}
\]  

(1.4)

where \( \delta \), known as the skin depth, defines the characteristic length in which the fields decay within the conductor. This is the well known classical skin effect in metals in the local limit, where the skin depth is much larger than the mean free path of the electrons.

Case of a Superconductor

In the case of a superconductor one has to recognize the fact that a large fraction of the conduction electrons have condensed into a lossless superfluid state, which at DC, will manifest itself as a zero resistance conductor. At finite frequencies however, the inertia of superfluid electrons prevents them from responding instantaneously to the oscillating fields, and then thereby can no longer short circuit the conductor; the remaining normal electrons will respond to the remaining field. It is clear then that an electrodynamic analysis of a superconductor should incorporate both the superconducting electrons and the normal electrons or more accurately, the quasiparticle excitations.

On this basis, in 1934 H. London [1] proposed a phenomenological model to describe the electrodynamics behaviour of superconductors which incorporated the two fluid model of Gorter and Casimir [2].

The two fluid model assumes that the electron system is composed of two components, the superfluid component with a density of \( n_s \), and the normal component with an electron density \( n_n \). London made the assumption that \( n_s + n_n = n_0 \) where \( n_0 \) is the superfluid density in the limit of \( T \rightarrow 0 \), as well as the density of normally conducting electrons above \( T_c \). Subsequently the total current density is the sum of the superfluid current \( \vec{J}_s \) and the normal fluid current \( \vec{J}_n \):

\[
\vec{J} = \vec{J}_s + \vec{J}_n.
\]
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The normal fluid current still obeys ohm’s law, where as the superfluid response is governed by the London equation

$$\frac{\partial \overrightarrow{J}_s}{\partial t} = \frac{n_s e^{*2}}{m^*} \overrightarrow{E}$$

(1.5)

where $e^*$ and $m^*$ are the charge and effective mass of the superfluid electrons. Taking the field oscillations to be $e^{i\omega t}$, the superfluid current takes the form

$$\overrightarrow{J}_s = \frac{n_s e^{*2}}{i\omega m^*} \overrightarrow{E}$$

(1.6)

$$= \frac{-i}{\omega \mu_0 \lambda_L^2} \overrightarrow{E}$$

(1.7)

where $\lambda_L = \sqrt{\frac{m^*}{\mu_0 n_s e^{*2}}}$ is the London penetration depth. The total current density, thereby reduces to

$$\overrightarrow{J} = \left( \sigma_n - \frac{i}{\omega \mu_0 \lambda_L^2} \right) \overrightarrow{E}$$

(1.8)

where $\sigma_n$ is the conductivity of the normal fluid electrons. One can see that unlike a normal metal where at low frequencies the conductivity is real, the superconductor exhibits a complex conductivity where the imaginary part is a manifestation of the lossless superfluid electrons. One can still use the same line of calculations performed for a metal to solve the wave equation, except that the conductivity $\sigma$ should be taken as a complex quantity

$$\sigma = \sigma_1 - i\sigma_2$$

(1.9)

where $\sigma_2$ is defined as

$$\sigma_2 = \frac{1}{\omega \mu_0 \lambda^2}.$$

Similar to the solution for a metal, the propagation constant of the electromagnetic waves inside the superconductor is found as

$$\kappa^2 = i\mu_0 \omega \sigma_1 + \frac{1}{\lambda^2} - \mu_0 \epsilon \omega^2.$$  

(1.10)

At the measurement frequencies presented in this thesis, the last term ($\mu_0 \epsilon \omega^2$) which is due to the displacement currents is very small and can be safely
ignored. Rewriting the first term in terms of the skin depth $\delta$ (eqn. 1.4) yields

$$\kappa^2 = \frac{2}{\delta^2} + \frac{1}{\lambda^2}. \quad (1.11)$$

This is an interesting form because it basically shows the contributions of the normal fluid and superfluid in the shielding of the fields from the interior of the superconductor. Except at temperatures extremely close to $T_c$, where the superfluid density is substantially reduced, the superfluid shielding is much more effective than that of the normal fluid. In other words $\lambda \ll \delta$ (or equivalently $\sigma_2 \gg \sigma_1$) and the propagation constant reduces to

$$\kappa = \frac{1}{\lambda}. \quad (1.12)$$

Therefore inside the superconductor, the electromagnetic fields decay with a characteristic length known as the magnetic penetration depth $\lambda$. For lead, a conventional superconductor, $\lambda(T = 0) \approx 300\text{Å}$ and for high temperature superconductors, $\lambda(T = 0) \approx 1000\text{Å}$. The normal state skin depth for these materials at 1 GHz, is of the order of few microns, which validates the above argument that the superfluid component is the dominant term in the propagation constant.

As can be seen from the propagation constant $\kappa$ in equation 1.10, the normal fluid contribution increases with frequency. Therefore at higher frequencies, a more rigorous analysis is required to account for contribution of each component. As will be discussed in the next chapter, measurements performed in this thesis work are all at microwave frequencies of about 1 GHz which is well into the low frequency limit. However, as part of the contribution of these measurements to the spectroscopy of high temperature superconductors performed in our laboratory, the data have been combined with higher frequency measurements. In those cases, one needs to consider the fact that the normal fluid component reduces the effective superfluid shielding of the fields. Self consistent calculations to take this matter into account will be presented in subsequent chapters.

The main focus of this thesis has been on precision measurements of the magnetic penetration depth, and we devote the next section to a discussion of the importance of this quantity in the field of superconductivity in general, and high temperature superconductivity in particular, we also discuss its role in providing some of the key information needed to pinpoint the nature of the superconducting state.
1.2 Magnetic Penetration Depth

As discussed in the previous section, at low frequencies the lossless part of the electromagnetic response of a superconductor is just the screening of the superfluid electrons with number density \( n_s(T) \) and effective mass \( m^* \). The screening length \( \lambda(T) \) is given by

\[
\lambda(T) = \left( \frac{\mu_0 e^2 n_s(T)}{m^*} \right)^{-1/2},
\]

therefore measurement of \( \lambda(T) \) provides a means of measuring \( n_s(T)/m^* \), the ratio of the superfluid density to the effective mass of the charge carriers.

It can be shown that the temperature dependence of the superfluid fraction, defined as \( x_s(T) = \lambda^2(0)/\lambda^2(T) \), is dependent only on the density of states through \( \lambda^2(0) \)

\[
\frac{\lambda^2(0)}{\lambda^2(T)} = 1 - \frac{2}{kT} \int_0^\infty d\omega \frac{N(\omega)}{N_0} [f(\omega)(1 - f(\omega))]
\]

where \( N(\omega) \) and \( N_0 \) are the density of states near the Fermi surface in the superconducting state and at the Fermi surface of the normal metal respectively, and \( f \) is the Fermi function.

Within a BCS type formalism, \( N(\omega) \) is determined by the superconducting gap \( \Delta(\vec{k}) \) which in general, due to anisotropic Fermi surfaces and \( \vec{k} \) dependent pairing interactions, may have a substantial dependence on \( \vec{k} \). In the case of \( \text{HiT}_c \) superconductors where the superconducting ground state is a spin singlet, the spatial part of the wavefunction must be even. In a truly isotropic system (no lattice) only even values of the pair orbital angular momentum are allowed \( l = 0, 2, 4 \cdots \) labelled s-wave, d-wave, g-wave etc. In a crystal lattice, \( l \) is no longer a good quantum number so that one must use the group-theoretic labels. The table below [5] shows the 4 singlet pairing states of a single plane with square symmetry, the approximate symmetry of most of the cuprates.
Figure 1.1: the four singlet irreducible representations possible in a single square $CuO_2$ plane (Annett et al. [5])

Figure 1.1 shows the shapes of representative gap functions[5]. We note that for $S^+$, any function that has the full symmetry of the lattice is allowed, and in particular the gap may change sign. The $B_{1g}$ and $B_{2g}$ states (informally called the “d-wave” states) $d_{x^2-y^2}$ and $d_{xy}$ break the symmetry of the lattice (as does the $A_{2g}$ state) and are therefore formally distinct from the $S^+$ (s-wave) states. However, for orthorhombic crystals there is no longer any distinction and one will always have mixtures of, for example, s and d.
There is now considerable experimental evidence that the predominant state is a "distorted" d-wave where the effect of orthorhombicity is mainly to make one set of opposing lobes somewhat larger than the other. This means that the nodes (positions where $\Delta(\vec{k}) \to 0$) may be shifted from the 45 degree positions.

Figure 1.2 a, b, c, d shows schematically the gap function for (a) isotropic s-wave, (b) moderately anisotropic s-wave, (c) d-wave and (e) an extreme case of anisotropic s-wave (sometimes called extended s-wave). Here we have used polar plots of energy, where the Fermi energy always gives a circle. Also we are assuming that the material is strongly 2 dimensional, with little dispersion in the $z$ direction, so that the nodes in the d-wave and extended s-wave case are line nodes. In Fig. 1.3 we summarize the results for the densities of states and the expected low temperature dependencies for $\Delta \lambda(T) = \lambda(T) - \lambda(0)$. Note that extended s-wave and d-wave states would give identical results. We have also shown the effect of impurities on the d-wave density of states: a finite density of states is produced at the Fermi level which results in $\Delta \lambda(T) \propto T^2$ instead of $T$ for the pure d-wave case [4].

Non-Local Effects

Possible non-local effects affecting the superfluid response embodied in $\sigma_2(T)$ or equivalently $1/\lambda^2(T)$ have been considered by Kosztin and Leggett [6]. Generally, in a strong type II superconductor where $\lambda(T = 0) \gg \xi_0$ the coherence length, non-local effects are negligible. However, in a clean anisotropic superconductor where the usual BCS expression $\xi_0 = v_f/\pi \Delta_0$ becomes $\xi(\vec{p}) = v_f/\pi |\Delta(\vec{p})|$, if $|\Delta(\vec{p})| \to 0$ at a node, the conditions for local response can be violated. Kosztin and Leggett go on to show that for a 2D Fermi surface and a clean d-wave superconductor, non-local effects may show up in the low temperature behaviour of $\lambda(T)$, but only when the applied field is along the [001] direction. None of the measurements in this thesis were taken in this geometry, so we do not expect to see such non-local effects.

There is the related issue of non locality in the response of the thermally excited quasiparticles which gives rise to $\sigma_1(T)$. It is known that at low $T$, the quasiparticle lifetimes imply rather long quasiparticle mean free paths in
Figure 1.2: Some examples of gap symmetries for 2D square lattice.
the ab plane, of order microns, which are larger than the London penetration depth (of order 0.1 or 0.2 microns). Therefore for microwave fields applied \( \perp \) the ab plane, the quasiparticles can easily move from the surface to an inner region not penetrated by the applied field, thereby producing non-local effects. On the other hand, for fields applied parallel to the ab plane, it is the mean free path in the c-direction compared to \( \lambda(T) \) that determines whether non-local effects are present or not. In fact, the mean free paths in the c-direction are very short, of order one lattice spacing. Therefore in our experiments where the microwave field are applied parallel to the ab plane, one expects non-local effects to be very small.
References


Chapter 2

Experimental Techniques

2.1 Surface Impedance

As it was discussed in the previous chapter, the electrodynamic properties of metals and superconductors are best described in terms of the complex conductivity (eqn. 1.9) \( \sigma = \sigma_1 - i\sigma_2 \). However, the experimentally accessible quantity is the complex surface impedance, defined to be the ratio of the tangential electric and magnetic fields (e.g. \( E_x/H_y \)) and written as \( Z_s = R_s + iX_s \), where \( R_s \) is the surface resistance and \( X_s \) the surface reactance. In the limit of local electrodynamics, the conductivity is related to the microwave surface impedance via

\[
Z_s(\omega) = \left( \frac{i\mu_0\omega}{\sigma_1 - i\sigma_2} \right)^{1/2}. \tag{2.1}
\]

In the normal state this local relation is valid if the mean free path of charge carriers is smaller than the classical skin depth. As mentioned in chapter one, in the superconducting state of high temperature superconductors, the small size of the coherence length compared to the penetration depth (\( \xi \ll \lambda \)), as well as the configuration which we have used to probe the response of the superfluid current on the surface of the material, guarantees the electrodynamics is local. In the normal state of a metal, where \( \sigma_1 \gg \sigma_2 \), Eq. 2.1 yields the classical skin effect relationship

\[
R_s = X_s = \left( \frac{\mu_0\omega}{2\sigma_1} \right)^{1/2} = \frac{1}{2}\mu_0\omega\delta. \tag{2.2}
\]

Thus, in the normal state, measurement of either the real or imaginary part of the surface impedance simply yields \( \sigma_1 \).

In the superconducting state, \( \sigma_2 \) arises from superfluid screening and it was shown that \( \sigma_2 = 1/\mu_0\omega\lambda^2 \) where \( \lambda \) is the London penetration depth.
Except at temperatures very close to $T_c$, $\sigma_2 \gg \sigma_1$, and it can be easily shown that

\[ R_s = \frac{1}{2} \mu_0^2 \omega^2 \lambda^3(T) \sigma_1(\omega, T) \]
\[ X_s = \mu_0 \omega \lambda(T). \] (2.3)

Thus, a measurement of the surface reactance $X_s(T)$ allows a direct determination of the London penetration depth. A measurement of $\sigma_1(T)$, on the other hand, requires both measurements of $R_s(T)$ and $\lambda(T)$. Note that in the data analysis, it is very convenient to use the exact expression 2.1 for the surface impedance, as it allows to analyze the superconducting and normal state data simultaneously as well as the temperatures very close to $T_c$ where the approximations 2.3 may not be valid.

At microwave frequencies, a standard way to measure $Z_s$ is by cavity perturbation techniques. If the sample under study is introduced into a microwave cavity resonator such that the fields inside the cavity are weakly perturbed then the change in the resonance frequency $f$, and the quality factor $Q$ of the resonator is given by

\[ \frac{\delta f}{f} - i \frac{1}{2} \delta(\frac{1}{Q}) = i \Gamma Z_s \]
\[ = -\Gamma(X_s - i R_s) \] (2.4)

where $\Gamma$ is a geometric factor which depends on the dimensions of the sample and the cavity resonator and also on the configuration of the fields which are being perturbed. Although in many cases a theoretical calculation of $\Gamma$ is possible, a direct determination of the calibration constant $\Gamma$ is normally carried out by measuring a known sample. As will be seen later, for our type of measurements where a conducting sample perturbs a magnetic mode, a metal with a well known or well measured resistivity is a suitable candidate for calibration purposes. In the subsequent sections, we first introduce the type of microwave cavity resonators used in this study and then will proceed with the cavity perturbation calculations appropriate for these setups.
2.2 Microwave Cavity Resonators: Loop-Gap Resonators

2.2.1 Motivation

Cylindrical type cavities are one of the most popular resonators employed for the measurements of microwave properties of materials. They are easy to build, can be operated at different modes to suit the experiment, e.g. electric or magnetic measurements, and more importantly, they have very high quality factors which are needed for measurement on very low loss materials. Indeed, measuring the surface impedance of superconducting materials in their superconducting state forces the use of high Q factors. However, there are disadvantages in using these type of resonators for magnetic penetration depth measurement. At low frequencies, the size of a cylindrical resonator is very large (e.g. $\sim 10^3 \text{ cm}^3$ at 1 GHz) and quite often there are restrictions on the size of the samples. For example, a typical volume of the highest quality single crystals of high temperature superconductors is no more than $\sim 10^{-5} \text{ cm}^3$, which is extremely small compared to the volume of a 1 GHz cylindrical resonator.

This difficulty is well known in NMR experiments where the resonance frequency is in the MHz range and in order to obtain a reasonable filling factor, a simple coil of order the size of the sample and resonated by a capacitor is used to pick up the response. Such a detection system however, has very low Q and therefore typically does not have enough sensitivity for our type of measurements.

Another difficulty with cylindrical type resonators is the background. Even for the lowest order modes which have the simplest configuration of the fields, it is not possible to perform a magnetic measurement and completely avoid the electric fields. The dielectric response of the sample or the sample holder may produce enough background to obscure the actual signal. In some cases, it may be possible to reduce the background significantly by using very low loss dielectric materials such as high purity sapphire plates as sample holder.

The above mentioned problems were the motivation to design loop-gap (or split-ring) resonators which are in a sense the microwave equivalent of an LC circuit [1] [2]. They are now widely used in NMR measurements where the resonators are small enough to obtain large filling factors[3], yet have
very high quality factors, comparable to cylindrical resonators. However, unlike cylindrical resonators, the field configuration is more like an $LC$ circuit where there is usually only one low frequency resonant mode consisting of a uniform magnetic field in the loop (inductor) and uniform electric field in the gap (capacitor) and they are well separated (except for some fringing of electric fields). This makes them suitable for pure magnetic or pure electric measurements by positioning the sample either in the loop or in the gap respectively.

Figure 2.1 shows the cross section of a few possible configurations for loop-gap resonators. In design (a), the loop is open at only one end which forms the gap, usually filled with a low loss tangent, high dielectric constant material such as high purity sapphire. Design (b) consists of two gaps and is also referred to as split-ring resonator. There is little difference between these two designs as far as their resonance characteristics is considered, however each has its own technical pros and cons. Design (c) is a two loop, three gap resonator, and unlike the first two designs has two distinct low frequency resonance modes.
2.2.2 Our design

Figure 2.2 shows the schematics of the loop-gap resonator used in this work. This resonator and its sample holder was designed by Dr. Walter Hardy specifically for the precision measurement of the magnetic penetration depth of high temperature superconductors. The resonator is made out of copper and later electroplated with lead-tin alloy so that at liquid He temperature, it is superconducting (the few percent tin in the plating solution slows oxidation of the lead). A copper resonator in this configuration has a Q of about 1000 at low temperatures, however the lead-plated resonator has Q of over 1 million at 1.2K. The left side of the loop has three threaded blind holes which allows the resonator to be bolted tightly onto its holding assembly displayed in figure 2.3. Inside the gap, a high purity sapphire plate is tightly held, which serves two purposes. First its high dielectric constant (about 10) increases the capacitance of the gap which further reduces the resonance frequency. Furthermore, ultra high purity sapphire has an extremely low loss tangent ($\sim 10^{-8}$), thereby allowing Q's in the range of a few million for the resonator. Finally, the strength of the sapphire allows the gap to be firmly held in place which minimizes the effect of mechanical vibrations (microphonics).

A drawback of this design is the existence of a joint between the left side of the loop and the mounting assembly. This is an electrical joint, and currents have to flow through it to complete the resonance circuit. It is therefore very important to make this a lossless superconducting joint by applying enough pressure on the bolts to basically fuse together the two lead-plated surfaces. To accomplish that (see figure 2.2) a wide groove has been cut into the bottom face of the left side wall to leave it with two narrow lips. Under pressure, these lips dig into the lead-plating of the opposite face. A poor joint will manifest itself as weak links in the resonance signal and lowers the Q of the resonator. In that case the assembly has to be taken apart, re-electroplated and assembled again. A good joint however, can lead to a high Q and a very stable resonance which can be used for a long period of time, as long as a few years.

The resonance frequency is sensitive to the thickness of the sapphire plate as well as its mounting on the support assembly. Over the years which the resonator has been used, its frequency has ranged from 900 MHz to 1.2 GHz. Initially a sapphire plate with thickness of 0.1 mm (0.004") was used, but was later replaced with a thinner plate, thickness of 0.05 mm (0.002") in order to lower the resonance frequency.
Figure 2.2: Upper: photo of the loop from the 1 GHz loop-gap resonator, sitting on a flat surface. The sapphire dielectric plate is visible under the right hand leg of the loop. The copper resonator is electroplated with lead-tin which explains its gray color. Lower: cross-sectional drawing of the resonator. The dimensions are in mm. The drawing is to scale except the thickness of the sapphire plate which is exaggerated for clarity. The solid rectangle inside the loop shows the location of the sample.
As can be implied from above discussion, precision machining of the loop is an absolute necessity for this structure to work and this would have not been possible without the effort of the skilled staff in the UBC Physics Department machine shop.

2.2.3 Calculation of resonance frequency

A common and simple way to estimate the resonance frequency of the loop-gap resonator is to model it as a resonant LC circuit with the loop and the gap being the inductor $L$, and the capacitance $C$, respectively. Ignoring the deviations of the magnetic field from that of a long solenoid, they are given by

$$C = \varepsilon_r \varepsilon_0 \frac{bw}{t} \quad L = \mu_0 \frac{aa_1}{b}$$

(2.5)
where \( \varepsilon_r \) is the relative dielectric constant of the material inside the gap, \( \varepsilon_0 \) and \( \mu_0 \) are the permittivity and permeability of vacuum and \( b \) is the length of the loop. The rest of the dimensions are shown in figure 2.2 and are summarized below.

\[
\begin{align*}
a &= 0.200'' = 5.08 \text{ mm} \\
a_1 &= 0.100'' = 2.54 \text{ mm} \\
b &= 0.450'' = 11.43 \text{ mm} \\
w &= 0.140'' = 3.55 \text{ mm} \\
t &= 0.002'' = 0.051 \text{ mm}.
\end{align*}
\]

For the above dimensions and taking \( \varepsilon_r = 10 \) for sapphire, \( L \) and \( C \) are found to be

\[
C \approx 7.1 \times 10^{-11} F \quad L \approx 1.4 \times 10^{-9} H
\]

and the resonance frequency

\[
f = \frac{c}{2\pi\sqrt{LC}} \quad \text{(2.6)}
\]

\[
f = \frac{c}{2\pi n} \left(\frac{t}{a a_1 w}\right)^{1/2}
\]

\[
\approx 500 \text{ MHz}.
\]

where \( c \) is the speed of light in vacuum, and \( n = \sqrt{\varepsilon_r} \) is the index of refraction of sapphire. The calculated frequency of 500 MHz is somewhat smaller than the actual operating frequency, 1000 to 1200 MHz. There are several approximations that have been made, all of which tend to result in a higher resonance frequency. The finite length of the resonator will reduce the inductance from the form given in eqn. 2.5, a better estimate of it can be found in [4],

\[
L = \mu_0 \frac{a a_1}{b} F(\varepsilon, k) \quad \text{(2.8)}
\]

\[
\approx 1.2 \times 10^{-9} H
\]

in which \( F = 0.871 \) is a polynomial in \( \varepsilon = \frac{a}{b} \) with its coefficients being functions of \( k = \frac{a_1}{a} \).

Another factor contributing to the increase of the resonance frequency is the cylindrical shield which is surrounding the resonator in order to stop the propagation of the fields. This will increase \( f \) by a factor of \( 1 + \frac{A_1}{A_2} \) where \( A_1 = 0.13 \text{ cm}^2 \) and \( A_2 \approx 2 \text{ cm}^2 \) are the cross sectional area of the resonator and the shield respectively [1].
2.3 Cavity Perturbation Methods Applied to Loop-Gap Resonators

In section 1, we showed that by perturbing the electromagnetic fields inside a microwave resonator, we can relate the surface impedance (and therefore the conductivity) of the material to the characteristics of the resonance, i.e. the resonance frequency \( f \) and the quality factor \( Q \). Moreover from equation 2.4 we find

\[
\frac{\delta f}{f} = -\Gamma X_s, \tag{2.9}
\]

\[
\frac{1}{2} \delta \left( \frac{1}{Q} \right) = -2\Gamma R_s. \tag{2.10}
\]

Therefore exclusion of the fields from the interior of the sample, either due to skin effect in the normal metal or the Meissner effect in the superconductor will result in a shift in the resonance frequency of the cavity. At the same time, microwave losses due to the flow of currents on the surface of the sample result in changes in the \( Q \) of the cavity.

Let's consider a more specific geometry shown in figure 2.4, where a very thin sample is placed in a uniform magnetic field. In this situation, the demagnetization effects are very small and therefore the magnetic field at the surface of the sample is almost equal to the applied field. If such a sample is placed in the uniform magnetic field of the loop-gap resonator described above, standard cavity perturbation calculations show that the change in the resonance frequency and \( Q \) of the resonator is given by [6]

\[
\frac{\delta f}{f} - i \frac{1}{2} \delta \left( \frac{1}{Q} \right) = \frac{1}{2 V_c} \left\{ 1 - \frac{\tanh(\kappa c/2)}{\kappa c/2} \right\}. \tag{2.11}
\]
where $V_s$ and $V_c$ are the volume of the sample and the effective volume of the cavity respectively and $c$ is the thickness of the sample. $\kappa$ is the propagation constant of the electromagnetic field in the sample and, as was calculated in chapter 1, is given by

$$\kappa = \sqrt{i \omega \mu \sigma_1 - i \sigma_2}$$

$$= \frac{1}{\lambda} \quad \text{(in the SC state } \sigma_1 << \sigma_2)$$

$$= \frac{1 + i}{\delta} \quad \text{(in the normal state } \sigma_2 = 0) \quad (2.12)$$

where $\lambda$ and $\delta$ are the penetration depth and skin depth respectively. Very close to $T_c$ where $\sigma_1$ and $\sigma_2$ could be comparable, one has to use the full form for $\kappa$ to avoid any errors. If the thickness of the sample is much larger than the penetration depth (or the skin depth in the normal state) the tanh term is 1 and the frequency shift from equation 2.11 is reduced to

$$\frac{\delta f}{f} = \frac{1}{2} \frac{V_s}{V_c} \left( 1 - \frac{2\lambda}{c} \right) \quad \text{superconducting state}$$

$$= \frac{1}{2} \frac{V_s}{V_c} \left( 1 - \frac{\delta}{c} \right) \quad \text{normal state} \quad (2.13)$$

Therefore the corresponding frequency shift is proportional to $c - 2\lambda$ in the SC state, and $c - \delta$ in the normal state, which is basically the volume of the sample minus the volume which has been penetrated by the fields. One might think that a measurement of the frequency shift should give the absolute value of $\lambda$. In practice however, this is extremely challenging if not impossible. Since typical single crystals have $c \geq 20\mu$ and $\lambda \approx 1000 \AA$, in order to extract the absolute value of $\lambda$ to within 10%, from a measurement of the excluded volume, one would need to know the thickness of the crystal to an accuracy better than 1/1000. In addition there are demagnetizing corrections and calibration factors that would also have to be known to this accuracy. Therefore one has to be content with only measuring the temperature dependence of the penetration depth, relative to some reference temperature. In our case, we take it to be the temperature of the liquid He bath $T_0 = 1.2K$. As the temperature of the sample is increased above the reference temperature, the field penetration increases (due to the decrease in superfluid density) which causes the frequency of the resonator to change.
Defining $\Delta f(T) \equiv \delta f(T) - \delta f(T_0)$ to be the frequency shift due to the change of the temperature of the sample and for the moment ignoring the thermal expansion effects which change the actual dimensions of the crystal, one finds

\[ \Delta f(T) = -\left(\frac{A_s f}{V_c}\right) \Delta \lambda(T) \]  

(2.14)

where $\Delta \lambda(T) \equiv \lambda(T) - \lambda(T_0)$ and $A_s$ is the area of the sample. This is a simple relation which shows the change in penetration depth is proportional to the measured frequency shift. The proportionality constant can be found by measuring a normal metal with known skin depth, as will be discussed at the end of this chapter.

One should notice, however, that the above relation is valid when the thickness of the sample is much larger than the penetration depth which may not hold very close to the transition temperature. In that case one should calculate $\Delta f(T) \equiv \delta f(T) - \delta f(T_0)$ from the full solution 2.11.

In equation 2.11 it is assumed that the field penetrates only through the face of the crystal and not from the sides. However, since the shielding currents loop around the sample and thereby run across the c-axis, there is a c-axis penetration depth. The electromagnetic problem for this case is now two dimensional and its solution is more complicated compared to one-dimensional case. Accounting for the contribution of $\lambda_c$, cavity perturbation leads to a more complicated equation [7]

\[ \frac{\delta f}{f} = \frac{1}{2} \frac{1}{Q} \left(1 - \frac{8}{\pi^2} \sum_{n=odd}^{\infty} \frac{2}{n^2} \left(\frac{\tanh(\gamma_n a/2)}{\gamma_n a/2} - \frac{\tanh(\kappa_n c/2)}{\kappa_n c/2}\right)\right) \]  

(2.15)

where $\gamma_n$ and $\kappa_n$ are the propagation constants of the field through the surface and the edge of the crystal respectively and in the superconducting state are given by

\[ \gamma_n = \frac{1}{\lambda_{ab}} \sqrt{\left(\frac{n\pi \lambda_c}{a}\right)^2 + 1} \]

\[ \kappa_n = \frac{1}{\lambda_c} \sqrt{\left(\frac{n\pi \lambda_{ab}}{c}\right)^2 + 1} \]

Again, if the dimensions of the crystal are much larger than the corresponding penetration depth, it can be shown that

\[ \frac{\delta f}{f} = \frac{1}{2} \frac{V_s}{V_c} \left\{1 - \frac{2\lambda_{ab}}{c} - \frac{2\lambda_c}{a}\right\} \]  

(2.16)
Finally, the frequency shift $\Delta f(T)$ due to the change in the temperature of the sample, ignoring thermal expansion effects, is given by

$$\Delta f(T) = -\left( \frac{A_s}{V} \right) \left\{ \Delta \lambda_{ab}(T) + \frac{a}{c} \Delta \lambda_c(T) \right\} \quad (2.17)$$

We see that the contribution of c-axis penetration depth is reduced by the aspect ratio of the crystal. For YBCO crystals with a typical width of 1-2 mm and thickness of 10-20 microns this ratio is of the order of 0.01. This will lead to less than 10% error in the measurements of optimally- or over-doped YBCO crystals if the c-axis contribution is ignored; however the correction can be as large as 50% for an underdoped crystal. In the next section we briefly describe the effect of thermal expansion of the sample and how ignoring them can lead to serious errors if one is measuring very thick crystals. In the section following that, we will describe a novel technique to utilize eqn. 2.17 for simultaneous measurements of the ab-plane and c-axis penetration depths.

### 2.3.1 Thermal Expansion Effects.

In many cases, it is imperative to correct for thermal expansion of the crystal itself. Consider the geometry of figure 2.4 where we have in mind a typical $H_iT_c$ crystal with $c \ll a, b$. It was shown that for $c/2\lambda \gg 1$, the frequency shift is given by

$$\frac{\delta f}{f} = \frac{V_s}{2V_c} \left[ 1 - \frac{\tanh(c/2\lambda)}{c/2\lambda} \right] \approx \frac{V_s}{2V_c} \left[ 1 - \frac{2\lambda}{c} \right] \quad (2.18)$$

Ignoring the thermal expansion effects, the temperature dependence of the frequency shift defined as $\Delta f(T) = \delta f(T) - \delta f(T_0)$, was given by eqn. 2.14. Taking the thermal expansion effects into account will however give

$$\frac{-V_c \Delta f}{A_s \lambda(T)} = \frac{\Delta \lambda(T)}{\lambda(T)} - \frac{c(T_0)}{2\lambda(T)} \frac{\Delta V_s}{V_s} - \frac{\Delta A_s}{A_s} \quad (2.19)$$

where $\Delta V_s = V_s(T) - V_s(T_0)$ and $\Delta A_s = A_s(T) - A_s(T_0)$ are the thermal expansion of the volume and area of the sample respectively. The second two terms in eqn. 2.19 are corrections to $\Delta \lambda/\lambda(T)$ due to thermal expansion. Since $\Delta V_s/V_s$ and $\Delta A_s/A_s$ are of similar magnitudes for YBCO, one sees that the second term dominates when $c/2\lambda \gg 1$, the usual situation. The effect of
Figure 2.5: Thermal expansion effects on the apparent penetration depth of a YBCO single crystal for various thicknesses. The curves are all derived from the measurement on a 15 µ thick crystal.

not making this correction is shown in Fig. 2.5 where the "apparent" $\Delta \lambda(T)$ is shown for crystals of thicknesses 15, 100, 200, and 500 µ. To produce this graph we have used real data for $\Delta \lambda_{ab}(T)$ in $YBa_2Cu_3O_{6.95}$ and the thermal expansion data of Kraut et al. [5]. It is clear that for thicker crystals, the corrections are very important and ignoring them could lead to artificial features.

2.3.2 Measurement of the anisotropy of $\lambda$

In the geometry of our measurements where the magnetic field is applied parallel to the ab-plane of the thin plate-like single crystals of YBCO, there is a contribution to the frequency shift from field penetration at the edge of the crystal where the currents flow in the c-direction (see Fig. 2.6). As obtained in eqn. 2.17, the observed frequency shift in the resonance frequency of the microwave cavity is

$$\Delta f(T) \propto \Delta \lambda_{ab}(T) + \frac{\alpha}{c} \Delta \lambda_c(T)$$  \hspace{1cm} (2.20)
where \( c \) is the thickness and \( a \) the width of the crystal. This expression shows that the relative contribution of \( c \)-axis penetration depth is reduced by the aspect ratio \( a/c \) of the crystal which can be as large as 100. However, it is well known that the HiT\( c \) materials are anisotropic with a range that widely varies among members of the cuprates family and is also highly dependent on doping concentration. In the case of YBCO it is observed that the ratio of the \( c \)-axis normal state resistivity near \( T_c \) to that of the \( ab \)-plane increases strongly with a decrease in doping. At optimal doping the ratio is about 50 and increases to about 1000 for \( O_{0.6} \). Also, the zero temperature penetration depth \( \lambda_0 \) shows a strong anisotropy. The \( ab \)-plane penetration depth \( \lambda_{ab,0} \) stays in the range of 1000 to 2000 \( \AA \) with doping, where as \( \lambda_{c,0} \) is about 1 micron for optimal doping and increases to 7 microns for \( O_{0.6} \). This shows that although for optimal or overdoped crystals it is safe to ignore the \( c \)-axis contribution to the total penetration depth, for underdoped samples it can be a large contribution and should be taken into account.

Figure 2.6 shows the technique we have developed to measure the anisotropy of \( \lambda \). Initially the crystal is measured in the usual way and equation 2.20 applies. Later the crystal is cleaved into \( n \)-pieces and then measured in the same configuration as the first measurement. This array of crystals still has the same \( ab \)-plane surface area and therefore \( \Delta \lambda_{ab} \) has not changed. However, the contribution of \( \lambda_c \) has been greatly increased. Except very close to \( T_c \) where \( \lambda_c(T) \) might be large enough to become comparable to the width of some of the needles (~ 0.1mm), the contribution of \( c \)-axis penetration depth is simply increased to \( n\Delta \lambda_c \). Simple algebra applied to the two sets of measurements then allows the extraction of both \( \Delta \lambda_{ab} \) and \( \Delta \lambda_c \). This method has been applied not only to underdoped YBCO crystals, but also to optimal and overdoped crystals and the \( c \)-axis penetration depth has been extracted. Figure 2.7 shows two of the crystals after they have been cleaved into pieces.
Chapter 2. Experimental Techniques

2.4 Experimental Setup

Figure 2.8 shows the sample holder assembly. The YBCO sample is mounted at one end of a 2 cm long, 2 mm wide and 0.1 mm thick sapphire plate. It is held in place with a minute amount of vacuum grease. The other end of the plate is mounted on a sapphire block to which is mounted a thermometer and a heater for controlling the sample temperature. The sapphire block is glued to a 1.5 cm long piece of thin wall quartz tubing, the other end of which is attached to a sapphire plug in a copper base which is at the liquid He bath temperature, i.e. 1.2 K. The quartz tubing provides the thermal isolation between the bath and the sample holder. This allows the sample to be easily heated and its temperature well regulated. Heating the sample to 100 K requires only about 50 μwatts of power.

Figure 2.9 shows all the components of the microwave system which is sealed with indium "o" rings and immersed in the liquid He bath. It can be seen how the sample, mounted on the sapphire plate, inserts into the loop-gap resonator. The resonator and the cylindrical shield around it remain at the liquid He bath temperature and its temperature stays very constant throughout the experiment. This is achieved by regulating the bath temperature using an additional heater and thermometer glued to the outside body of the cylindrical block. As the temperature of the sample is increased, the bath regulator compensates for the additional heat deposited into the bath, keeping the bath temperature constant.
Figure 2.8: Sample holder assembly. The YBCO single crystal is mounted at the end of a thin sapphire plate.

Figure 2.9: The Full assembly of the loop-gap resonator and sample holder.
2.5 Measurement Techniques

A standard technique for measuring the characteristics of a microwave resonator is by the transmission method. In this method a microwave signal is applied through the input coupling of the resonator and the transmitted signal is detected at the output. The response of the cavity is measured by sweeping the frequency around the resonance. A Lorentzian fit to the response allows the center frequency and the Q to be calculated. For our loop-gap resonator, this method of detecting the resonance frequency has an accuracy of about 1 or 2 Hz. For typical YBCO crystals with about 1 mm$^2$ area, this translates into about 2 Å sensitivity for penetration depth. Given that in YBCO the change in penetration depth at low temperatures is of the order of a few angstroms per kelvin, the transmission method does not have the sensitivity desired for accurate measurements of $\Delta\lambda(T)$.

A second method, called the oscillator technique, was used by Dr. W. Hardy for measurements on HiT$_c$ superconductors and allows a continuous monitoring of the frequency of the resonator. When used with the loop-gap resonators described here, the stability over 1 minute reached about 0.1 Hz, thereby increasing the sensitivity of the penetration depth measurements by a factor of 10 to about 0.2 Å. Below we describe this technique in more detail.

2.5.1 Oscillator Method

The oscillator technique, illustrated in figure 2.10 is most suitable when the sample is in the superconducting state at temperatures where the sample losses are too small to cause any significant change in the Q of the cavity. In this method, unlike the transmission, there is no synthesizer applying a microwave signal to the cavity. Instead, the cavity becomes part of a feedback loop. Given enough gain the remaining condition for oscillations is that the phase around the loop is zero modulo $2\pi$. This condition is achieved by using a phase shifter which functions by varying the path length of the loop. A combination of microwave amplifiers, attenuators and limiter is used to control the signal to an appropriate value. In general the power at the input to the cavity is higher by about 20 db compared to the operating level used in the transmission method. However, no power dependence has been observed in measurements on YBCO single crystals grown at UBC. Once the circuit is oscillating, the phase shifter is then fine tuned to maximize the amplitude of the oscillations, which insures that the loop is right at the
Figure 2.10: Schematics of the oscillator loop electronics.

resonance frequency of the cavity. To monitor the frequency, a directional coupler is used to sample part of the signal, which is then mixed with a CW source set at about 100 kHz above the resonance frequency. The beat frequency is then easily measured using a frequency counter and monitored on a chart recorder or computer.

The stability of the oscillator is mainly related to the stability of the phase in the oscillating loop which in turn is very sensitive to the path length. Therefore care has be taken to stabilize the effective length of the loop. The room temperature electronics are all mounted and secured on an aluminum plate whose temperature is regulated via water lines under the plate in which water from a temperature regulated bath circulates. Rigid coaxial cables are used rather than flexible ones in order to keep their length constant. A major component to the path comes from the coaxial lines which carry the microwaves into the liquid He dewar. The temperature gradient across these cables varies as the liquid nitrogen and helium levels change with time. This causes a drift in the frequency. However, as long as the drift is relatively steady, one can still measure the frequency shift without a significant loss in sensitivity. Another point worth mentioning is the role of the Q of the cavity in the performance of the oscillator loop. There is a phase shift in the microwave signal as it is transmitted through the cavity resonator. If the signal is exactly at its resonance, the phase shift is zero, but can vary from $-90^\circ$ to $+90^\circ$ over the bandwidth of the resonance. Therefore the higher
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the Q (in other words the sharper the resonance), this phase shift happens over a narrower range of frequencies which means that the frequency of the oscillator loop is less sensitive to phase instabilities in the loop. This was in fact observed during a period of about two years, when the Q of the resonator was about $4 \times 10^6$, three times larger than its usual value. In that period, the oscillator loop was much more stable and easier to operate. This also explains why the oscillator method is best used at temperatures where there is negligible change in the Q of the cavity due to the sample losses. For our YBCO single crystals where the superconducting transition is only about 0.2 K wide, and the losses are extremely low, the oscillator method can be reliably used over the whole superconducting region up to about 0.2 K below $T_c$.

Figure 2.11 shows two traces of the chart recorder monitoring the frequency of the oscillator loop. The small horizontal divisions on the chart are equivalent to 1 HZ, and it can be seen that in the trace on the left, the frequency is stable to about 0.2 Hz over the length of the chart which is about 10 minutes. In the second trace, a steady drift is present, yet stable enough to still have resolution within fraction of 1 Hz. On both traces, frequency shifts can be observed when the temperature of the sample is changed from the base to say 2K, kept at that temperature for about 30 seconds to have a good reading of the frequency and then back to base temperature. In fact one of the advantages of the oscillator method compared to the transmission method is that it allows a continuous visual inspection of the resonance frequency. This allows one to pick stable periods in which to vary the sample temperature and also helps in recognizing the faulty data.
Figure 2.11: Stripchart recorder traces of the oscillator loop frequency as a function of time as the temperature of the sample is changed from the base temperature to various higher temperatures. Time increases in the vertical direction and each of the small divisions in the horizontal direction corresponds to a 1 Hz change in frequency. In the LH trace, the long time drift of the oscillator is nearly negligible. In the RH trace, there is substantial drift. Each trace is about 10 minutes in length.
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References


Chapter 3

Study of Microwave Electrodynamics in YBa$_2$Cu$_3$O$_{7-\delta}$ Single Crystals

3.1 Surface Impedance Studies of YBCO

Introduction

The microwave surface impedance has played an important role in sorting out the nature of the high $T_c$ superconducting state. It has provided crucial information on both the temperature dependence of the superfluid density and on the conductivity of the thermally excited quasiparticles in the superconducting state. Information on the real part of the conductivity and the penetration depth is obtained from the real and imaginary parts of the surface impedance $Z_s = R_s + iX_s$, where the real part is the surface resistance, and the imaginary part is the surface reactance. In the superconducting state the conductivity can be expressed as $\sigma(\omega, T) = \sigma_1(\omega, T) - i/\mu_0\omega\lambda^2(T)$ where the imaginary term is the inductive response of the superfluid and the real term is governed by absorption processes [1]. In the limit of local electrodynamics the surface impedance can be calculated from this using

$$Z_s(\omega) = \left(\frac{i\mu_0\omega}{\sigma_1 - i\sigma_2}\right)^{1/2} \quad (3.1)$$

and except very close to $T_c$, this leads to two simple expressions:

$$R_s = \frac{\mu_0^2\omega^2\lambda^3(T)\sigma_1(\omega, T)}{2} \quad (3.2)$$

and

$$X_s(T) = \mu_0\omega\lambda(T). \quad (3.3)$$
So, the surface reactance gives a direct experimental measure of the penetration depth, and thus the superfluid density. The surface resistance is somewhat more complicated since it is essentially a measurement of the absorption processes occurring within the depth that the microwave fields penetrate, and thus depends on both $\sigma_1(\omega, T)$ and $\lambda(T)$. After discussing the experimental techniques used to measure these two quantities, they will each be discussed turn.

**Experimental**

All of the crystals studied here were grown by a flux method in yttria stabilized zirconia crucibles [2]. Corrosion of these crucibles leads to impurity levels in the samples of order 0.1%. Crystals used for the microwave measurements were between 10 and 50 $\mu$m thick and were cleaved into rectangular shapes, typically 1-2 mm$^2$ in area. The samples were mechanically detwinned and subsequently reannealed in order to set the oxygen doping level.

Since these crystals are too small to perform sensitive cavity perturbation measurements of the surface impedance in the 1-5 GHz range with cylindrical resonators, superconducting split-ring resonators are used in a variety of measurement geometries [3, 4]. For measurements of the penetration depth, the sample is mounted on a sapphire plate and held fixed in the center of a loop-gap resonator, with the microwave magnetic field lying in the ab-plane of the thin crystal. Measurements of shifts in the resonant frequency then provide a direct measure of changes in the penetration depth as the sample temperature is varied. This geometry avoids systematic errors associated with sample motion and large demagnetization factors, allowing for precision measurements of the temperature dependence of the penetration depth relative to its value at a base temperature, usually 1.3 K ($\Delta \lambda(T) = \lambda(T) - \lambda(1.3K)$). The absolute value of $\lambda(0)$ can not usually be determined with this technique, so we instead use far infrared measurements to determine the absolute value of the penetration depth at low temperatures [5, 6]. One complication of this technique is that it mixes in a contribution from the temperature dependence of the c-axis penetration depth. For instance, with the field lying in the b direction in a thin platelet the frequency shift is given by $\Delta f = K[a\Delta \lambda_a + c\Delta \lambda_c]$ where $\lambda_a$ is the penetration depth for currents running in the a direction, $\lambda_c$ is the penetration depth for currents running in the c direction, and $a$ and $c$ are the crystal's dimensions in the a and c directions, respectively. Although the
contribution from $\lambda_c$ is small for a thin platelet, it is not negligible because $\lambda_c$ is typically much larger than $\lambda_a$. This complication can, however, be exploited to measure $\lambda_c$. Cleaving the plate into several thin needles multiplies up the contribution from the c-axis, so that measurements of the frequency shift before and after cleaving allow $\lambda_c$ and $\lambda_a$ to be separated.

Measurements of the surface resistance have been performed using cavity perturbation of a split-ring resonator at 3.8 GHz in which the surface resistance is determined from the change in $1/Q$ of the resonator when the crystal is inserted into it. The usual measurement geometry involves microwave magnetic fields applied perpendicular to the ab-plane, so the measurements are a combination of a and b axis surface resistance, without contamination from the c direction. Even with the high sensitivity of a superconducting split ring resonator, the microwave surface resistance is so low at this frequency that the Q of the resonator typically only changes by 1 to 10 % when the sample is inserted. Measuring these low losses requires repeated insertion and removal of the sample from the cavity at each measurement temperature. Careful attention must be paid to reducing microphonics because slight vibration of the sample inside a high Q resonator leads to rapid modulation of the resonant frequency that can spoil the Q measurement. Also, at the lowest surface resistance levels, nonperturbative effects must be taken into account. When a sample is inserted into the split ring the slight rearrangement of the microwave fields can lead to small changes in the microwave losses in the cavity walls. This effect is accounted for by measuring identically sized samples of Pb, which has a low and well known microwave surface resistance at low temperature and frequency.

Penetration Depth

Fig. 3.1 shows the measured values of $\Delta \lambda(T) = \lambda(T) - \lambda(1.3K)$ for all three crystal axes and at three different oxygen doping levels. Both $\Delta \lambda_a$ and $\Delta \lambda_b$ have a nearly linear temperature dependence at low temperatures for all three of the doping levels that we have tried. We have found that there is some sample to sample variation in the degree of curvature below 4 K, a problem which might be attributed to the residual impurity level in these samples. The variation from sample to sample does suggest that the curvature at low temperatures is not intrinsic behaviour, but higher purity samples will have to be measured to make certain that it is simply an impurity problem.
Figure 3.1: $\Delta \lambda(T)$ versus $T$ for the a, b, and c directions for three different oxygen doping levels in $YBa_2Cu_3O_x$. Most of the data points correspond to more than one sampling of the frequency shift, but the variation in the values is so small they appear as single points. For the c direction, which involves the difference of measurement for the whole crystal versus the cleaved crystal, the multiple points can be seen as separate.
Figure 3.2: The superfluid fraction, $\lambda^2(0)/\lambda^2(T)$, extracted from the data of Fig. 3.1 along with infrared determinations of $\lambda(0)$. 
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Figure 3.3: The superfluid fraction versus reduced temperature for three different doping levels of YBa$_2$Cu$_3$O$_x$; x=6.60 (circles), x=6.95 (squares), x=6.99 (triangles). In both the a and c directions, the temperature dependence of the superfluid fraction is largely independent of hole doping level in this range.

The very large change in the magnitude of $\Delta \lambda_c$ as a function of doping level reflects the large change in the absolute value of the c-axis penetration depth. Far infrared measurements indicate that $\lambda_c(0)$ increases from 1.1 $\mu$m to 6.5 $\mu$m upon deoxygenating from $O_{6.95}$ to $O_{6.60}$.

The difference between the behaviour of the penetration depth within the ab plane and along the c-axis is more apparent in the plots of $\lambda^2(0)/\lambda^2(T)$ shown in Fig. 3.2. $\lambda^2(0)/\lambda^2(T)$ is constructed from the microwave measurements of $\Delta \lambda(T)$ coupled with the far infrared measurements of $\lambda(0)$ and provides a relatively direct measure of the superfluid fraction. For all of the oxygen dopings that we have studied; underdoped, optimally doped, and slightly overdoped, the superfluid fraction decreases linearly with increasing temperature in both the a and b directions. When the temperature scale is normalized by $T_c$ the overall temperature dependence in the a direction (currents perpendicular to the CuO chains) is remarkably independent of doping, as is shown in Fig. 3.3. In the b direction the superfluid fraction also varies
Figure 3.4: Ni substitution at the 0.75% and 1.4% level and Ca substitution at the 2% level do not significantly affect the temperature dependence of the penetration depth.

linearly with temperature at low temperatures, but its slope evolves as a function of doping, being quite close to the a-axis curve in $O_{6.60}$, and somewhat steeper at higher hole doping levels.

The c-axis superfluid fraction is quite different, with a very flat temperature dependence at low temperatures and no clear sign of linear temperature dependence. It is perhaps even more surprising that the overall behaviour of the c-axis penetration depth shown in Fig. 3.3 does not seem to change much with the oxygen doping level, even though $\lambda_c(0)$ changes by a factor of 6 through this doping range [5].

The effects of various cation substitutions on the temperature dependence of the penetration depth have been extensively studied, particularly Ni and Zn which substitute for Cu in the YBCO structure. Fig. 3.4 shows that Ni impurities, which can occupy both the plane and chain Cu sites, have very little effect on the temperature dependence of the penetration depth in the ab-plane. The variation seen in Fig. 3.4 is within the variation seen from sample to sample in our nominally pure crystals. This result contrasts interestingly with studies that indicate that somewhat higher levels of Ni
impurities have a very large effect on the magnitude of the penetration depth [7]. Ca impurities, which occupy the Y site lying between the CuO$_2$ bilayers, also seem to have very little effect on the temperature dependence of the penetration depth. Also, if one regards oxygen vacancies in the CuO chains as being a defect, then the oxygen doping results shown in Fig. 3.1 indicate that oxygen vacancies in the chains do not strongly affect the temperature dependence of the penetration depth in the ab plane.

Zn substitution for Cu in the CuO$_2$ planes is the only defect that we have found so far that does have a strong effect on the temperature dependence of the penetration depth. Early studies of the effect of Zn indicated that the penetration depth at low temperatures changed from linear in T to T$^2$ with a substitution of only 0.3 % [8, 9] and this change in the power law has been attributed to the effects of a unitary scatterer in a d-wave superconducting state [10]. Within this model of a dirty d-wave superconductor, it has been suggested that the difference between Ni and Zn substitution might result from Zn acting as a unitary scatterer, but Ni acting as a weaker, Born
scatterer. The $T^2$ behaviour that is also seen in many thin films might then also be attributed to some strongly scattering defect, but the identity of this defect, or defects, has not been determined.

Fig. 3.5 shows this evolution towards quadratic temperature dependence upon going from a nominally pure $YBa_2Cu_3O_{7-\delta}$ crystal, through 0.15 % Zn substituted, to a crystal with 0.31 % Zn substitution. More recent measurements of samples with 1 % substitution of Zn for Cu complicate this picture. At this higher impurity level the penetration depth develops a weak, non-monotonic temperature dependence; $\Delta \lambda(T)$ starts to turn up again as temperature is decreased below 3 K. If the behaviour of $\Delta \lambda(T)$ is interpreted as a measure of normal fluid density, then this result indicates that at the lowest temperatures measured, the superfluid density starts to decrease slightly with decreasing temperature.

Surface Resistance

The penetration depth provides a rather straightforward measure of the superfluid density since the superfluid density is directly responsible for the measured screening of the microwave fields. Surface resistance is somewhat more complicated since it is essentially the absorption of microwave power within the penetration depth of the fields and thus depends both on the screening and the absorption processes going on within that screening depth. However, $\lambda(T)$ mainly influences the temperature dependence of $R_s(T)$ close to $T_c$ where the rapid drop in the screening length leads to a precipitous drop in surface resistance just below $T_c$. At lower temperatures the behaviour of $R_s(T)$ is largely governed by the temperature dependence of the conductivity $\sigma_1(\omega,T)$. In particular, the asymptotic behaviour of $R_s(T)$ at low temperatures is essentially the asymptotic behaviour of $\sigma_1(\omega,T)$.

Fig. 3.6 shows the low loss region of the surface resistance in the superconducting state for two different samples of nominally pure $YBa_2Cu_3O_{6.95}$. The broad peak in $R_s(T)$ for the pure sample has been studied in detail at a number of frequencies and in a large number of samples (see ref. [1] and references cited therein). It reflects a large peak in the temperature dependence of $\sigma_1(\omega,T)$ and it has been found that the height of this peak in the temperature dependence diminishes with increasing frequency; it is substantially smaller at 35 GHz [9] and eventually disappears altogether in the THz frequency range [11]. The picture that has emerged from this is that as the
temperature falls below $T_c$ the conductivity spectrum $\sigma_1(\omega)$ becomes sharply peaked at low frequency. In the normal state, the width of the conductivity peak is of order $2k_B T$, lying in the far infrared, but by 30 K the width of the peak is roughly 35 GHz - a collapse in the width of almost a hundredfold. This dramatic change has been interpreted as a collapse in the scattering rate of the thermally excited quasiparticles below $T_c$ [12]. Since this suggests that the inelastic scattering that dominates the normal state transport properties is drastically diminished, then the conductivity in the superconducting state should become very sensitive to scattering by impurities. This is clearly illustrated in Fig. 3.7 where it is shown that 0.75% substitution of Ni for Cu is sufficient to completely eliminate the broad peak in $R_s(T)$. Conversely, the presence or absence of a peak in $R_s(T)$ can give some measure of the presence of scattering centers in a sample.

The asymptotic low temperature behaviour of the surface resistance has been more problematic, because the losses being measured are very low and
Figure 3.7: At 0.75 % substitution (triangles) Ni completely suppresses the broad peak in the 3.8 GHz surface resistance and at 1.4 % (solid boxes) the overall surface resistance begin to increase in magnitude, perhaps due to the effect that high Ni concentrations have on the absolute value of λ. For all Ni concentrations studied, the surface resistance varies linearly with temperature at low temperatures.

because there seems to be a substantial degree of sample variation. Like the penetration depth, the surface resistance seems to be nearly linear below 30 K, with a sample dependent curvature and residual loss at low temperatures. Earlier measurements at 35 GHz also showed a linear temperature dependence, with a much greater signal to noise ratio because of the substantially larger loss at higher frequencies [9, 13]. The measurements at 35 GHz also tended to exhibit somewhat less sample dependence in the curvature and residual loss at low temperatures. However, 35 GHz is not strictly in the low frequency limit, since we have already determined that the conductivity spectrum at low temperatures has a width of order 35 GHz. Thus, measurements at a few GHz are important if one is trying to determine the behaviour in the low frequency, low temperature limit.

Although Fig. 3.7 indicates that Ni impurities introduce sufficient scat-
Figure 3.8: Like Ni impurities, Zn quickly suppresses the peak seen in the surface resistance of pure samples at 3.8 GHz. However, Zn radically changes the temperature dependence at low temperatures, giving rise to an increasingly large upturn in $R_s$ as the impurity concentration goes from 0.15 % (triangles), through 0.31 % (diamonds) to 1 % (solid boxes). Scattering to suppress the broad peak in the surface resistance, they seem to leave the linear temperature dependence of the surface resistance intact, much as Ni does not seem to affect the temperature dependence of the penetration depth. At 1.4 % Ni substitution, the overall magnitude of the surface resistance is larger than it is at 0.75 %, which may be due to an overall increase in the magnitude of $\lambda$, as suggested by the Ni substitution studies of Ulm et al. [7]. A beneficial product of this increase in the overall surface resistance is that the linear temperature dependence is particularly apparent in the sample with 1.4 % Ni substitution.

A study of the effects of Zn substitution on the surface resistance is summarized in Fig. 3.8. Like Ni, Zn introduces sufficient scattering to suppress the broad peak in the surface resistance. However, Zn substitution has more drastic effects on $R_s(T)$ at low temperatures. Below 4 K, the microwave loss turns upwards, particularly strongly at doping levels of 0.31 and 1 %. This
to some extent mirrors the effect that Zn substitution has on the penetration depth. This upturn in the microwave loss is completely absent in the earlier 35 GHz measurements \[9\], where the surface resistance was found to have a quadratic temperature dependence with no sign of non-monotonic behaviour. This indicates that this peculiar behaviour at low temperatures in both the penetration depth and the 3.8 GHz surface resistance involves an absorption process on an energy scale smaller than 1 K. At the present time, there is not sufficient spectroscopic information to say whether or not this feature is peaked at zero frequency or at some finite frequency.

**Discussion**

It has been pointed out throughout this work that there is sample dependent behaviour, particularly below 4 K, in both the penetration depth and the surface resistance. The strong effect that Zn has on the low frequency, low temperature electrodynamics sheds some light on this problem. A particularly severe example of sample dependence is shown in Fig. 3.9. The two samples used for the surface resistance and penetration depth measurements shown in Fig. 3.9 were both from the same batch of crystals with 0.31 % Zn substitution and both samples had the same \( T_c \), as observed in the microwave measurements, which indicates that the overall Zn concentration really is the same in both samples. However, the low temperature behaviour is strikingly different. One of the crystals has a much larger upturn in the microwave loss at low temperatures and strong non-monotonic temperature dependence of the penetration depth. The sample with the smaller upturn in the surface resistance has a monotonic penetration depth that varies as \( T^2 \). It is not yet clear what the origin of this difference is, but in light of this result it is perhaps not surprising that there is some small variation from sample to sample in our nominally pure crystals.

Despite the caveat about sample dependent curvature below 4 K, all of the results that we have obtained so far in detwinned crystals over a wide range of oxygen doping indicate that the penetration depth has a predominantly linear temperature dependence in both the a and b directions in \( YBa_2Cu_3O_x \). In fact, as is shown in Fig. 3.3, the a axis penetration depth is strikingly insensitive to oxygen content when plotted as a function of reduced temperature. Since the a axis is perpendicular to the CuO chains, this indicates that the penetration depth for the CuO\(_2\) planes has a temperature
Figure 3.9: An extreme case of sample variation is shown here for two samples of YBa$_2$Cu$_3$O$_{6.95}$ with 0.31 % Zn substitution (open and filled squares are two different samples). The sample with the larger upturn in the 3.8 GHz surface resistance has non-monotonic behaviour in the penetration depth at low temperatures.
dependence that is completely insensitive to the large changes in the normal state properties of $YBa_2Cu_3O_x$ that occur when the hole doping is taken from near the optimum value down into the underdoped regime. Whatever factors control the quantitative behaviour of the superfluid density are apparently insensitive to the changes in the degree of c axis coupling and the opening of the normal state pseudogap observed in underdoped samples. It is even more surprising that these changes in the normal state c axis properties are also not accompanied by large changes in the behaviour of the c axis penetration depth. The c axis penetration depth is different from the in-plane penetration depth, but just as for the in-plane properties, its temperature dependence is not strongly affected by the degree of doping.

The linear temperature dependence of the penetration depth has been attributed to a gap function that has lines of nodes [4], suggesting a d-wave superconducting order parameter. Within models of the effect of impurities on the penetration depth of a d-wave superconductor, the strong effect that Zn substitution has on the temperature dependence of the penetration depth has been attributed to the effects of unitary scattering, with other impurities such as Ni being Born scatterers. This explanation is in accord with other measurements such as NMR studies which indicate that Zn substitution produces a significant density of states at the Fermi energy [14]. However, the details of this model of Zn impurities must now also come to terms with the non-monotonic temperature dependence seen at low frequencies in both the penetration depth and surface resistance of samples with relatively high Zn doping.

The ab plane surface resistance of $YBa_2Cu_3O_{6.95}$ also seems to have a nearly linear temperature dependence except when the crystal contains Zn impurities. This temperature dependence, however, is at odds with the present calculations of the microwave conductivity, which predict a quadratic temperature dependence [15]. The surface resistance of those samples (both pure and Ni doped) that exhibit the lowest residual microwave loss does seem to approach the zero temperature limit predicted by P.A. Lee for a d-wave superconductor [16], but this limit has still not been strongly tested because the measurement sensitivity is comparable to the magnitude of the theoretical prediction [1]. The lowest loss samples do typically have the most clearly linear temperature dependence of the surface resistance, so there is no evidence yet of a sample that has surface resistance with quadratic temperature dependence that approaches the zero temperature value expected for a d-wave superconductor. Thus, the low temperature behaviour of the surface
resistance persists in being a puzzle that has not been completely solved.

References


3.2 A Comparison of the Influence of Ni and Zn Impurities on the Electromagnetic Properties of \( \text{YBa}_2\text{Cu}_3\text{O}_{6.95} \)

Introduction

One of the focal points of research on high \( T_c \) superconductors, the nature of the pairing state, can be investigated by experimental techniques that are sensitive to the spectrum of low-lying excitations in the superconducting state. However, the small coherence length of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) gives rise to substantial complications for the experimental techniques traditionally used to probe the superconducting pairing state. Tunnelling and far infrared absorption, the two techniques that usually give the most direct and detailed information on a superconductor's energy gap and spectrum of low-lying excitations, are still subjects of controversy when applied to this high \( T_c \) compound. Tunnelling measurements are difficult in a material with a coherence length that is comparable to the lattice spacing, and measurements of the energy gap by various tunnelling techniques remain controversial, particularly in \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) where the results depend a great deal on the type of tunnelling technique used[1]. The short coherence length also guarantees that pure \( \text{YBa}_2\text{Cu}_3\text{O}_{6-\delta} \) is in the clean limit which makes it difficult to measure an energy gap by far infrared techniques[2]. Infrared measurements are further complicated by the presence of the mid-infrared absorption band and phonon anomalies that are the dominant features of the low frequency optical conductivity[3].

The high critical temperature complicates many other measurements that, in principle, can be used to help identify the superconducting pairing state. The temperature dependence of thermal conductivity, ultrasonic attenuation, and heat capacity can provide information on the thermally excited quasiparticles in the superconducting state. For instance, the presence of an s-wave BCS energy gap manifests itself as an exponentially activated temperature dependence in all of these quantities at temperatures well below \( T_c \). Observation of power laws at low temperature would instead suggest a pairing state with nodes in the gap or gapless superconductivity. In \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \), however, in the temperature range of interest for probing the electronic excitations, these properties are all strongly influenced by phonon
contributions[4].

All of these difficulties make measurements of the low frequency electromagnetic properties of YBa$_2$Cu$_3$O$_{7-\delta}$ particularly important. At microwave frequencies the surface impedance, $Z_s = R_s + iX_s$, where $R_s$ is the surface resistance and $X_s$ is the surface reactance, is the measurable, complex quantity that characterizes the electromagnetic properties of a superconductor. The surface reactance measures the screening of fields by the superconducting condensate and provides a direct measure of the London penetration depth via (in MKS units) $X_s(T) = \mu_0 \omega \lambda(T)$. The penetration depth can also be measured by magnetization and $\mu$SR techniques. The temperature dependence of $\lambda(T)$ determined from any of these techniques can provide information on the pairing state, but the measurements to date have been highly controversial. $\mu$SR is one of the few techniques that can measure the absolute value of $\lambda(0)$, but measurement of the temperature variation of $\lambda$ has been complicated by sample dependencies[5, 6, 7, 8]. Another complication is that the muon relaxation rate is really a measure of field distribution in the vortex state, and some modelling of the vortex state is required in order to extract $\lambda(T)$. The degree to which this modelling affects the penetration depth extracted from $\mu$SR measurements is still an active area of study. Although the problems of sample dependence and modelling of the $\mu$SR lineshape are still being resolved, the most recent measurements, of crystals similar to the ones used for the measurements described in this article, indicate a linear temperature dependence for the penetration depth below 30 K[7].

Magnetization measurements of aligned powders of YBa$_2$Cu$_3$O$_{7-\delta}$ often indicate a nearly quadratic temperature dependence for $\lambda(T)$ in the ab-plane[9, 10]. Kinetic inductance measurements of the penetration depth in thin films of YBa$_2$Cu$_3$O$_{7-\delta}$[11] were also ultimately shown to be consistent with a quadratic temperature dependence in the penetration depth at low temperatures[12]. Early magnetization measurements of a single crystal of YBa$_2$Cu$_3$O$_{6.95}$ did not have sufficient precision to clearly discern the asymptotic behaviour of $\lambda(T)$ at low temperature[13], but a recent magnetization measurement of a Tl$_2$Ba$_2$CaCu$_2$O$_8$ crystal showed a dominant linear term[14]. A very large body of microwave measurements of YBa$_2$Cu$_3$O$_{7-\delta}$ has been plagued by sample dependence and linear[15], quadratic[16, 17, 18, 19], and exponentially activated[20] asymptotic behaviour have all been reported, a nearly quadratic term being the most commonly observed in thin films. Recently, a distinctly linear term in $\lambda(T)$ has been observed in YBa$_2$Cu$_3$O$_{6.95}$.
crystals and it has been suggested that the $T^2$ term and sample dependence observed in thin films is the result of point defects or grain boundaries\cite{15}. One possible explanation of a linear $\lambda(T)$ is a d-wave pairing state with line nodes in the gap function\cite{12}. It is well known on theoretical grounds that strong potential scattering by defects can easily push such a superconductor into the gapless regime where a quadratic rather than linear term would be observed\cite{21, 22}. Therefore, both the troublesome sample dependence in thin films and the possibility that YBa$_2$Cu$_3$O$_{7-\delta}$ might be a d-wave superconductor make it clear that studies of $\lambda(T)$ in carefully grown crystals with deliberately introduced defects are essential in this field.

The crucial role that defects play in the microwave properties of YBa$_2$Cu$_3$O$_{6.95}$ has already been demonstrated for the surface resistance\cite{23, 24, 25, 26}. Just as in the case of $\lambda(T)$, $R_s(T)$ in the crystals is qualitatively different from that observed in films. Whereas high purity crystals have a relatively high surface resistance with a broad peak near 40 K in the temperature dependence\cite{8, 27, 28}, some high quality films exhibit a loss that is lower and that decreases monotonically with temperature. On the other hand, films also tend to suffer from substantial variation from sample to sample\cite{18, 23, 29}. The high loss and non-monotonic temperature dependence in single crystals have been attributed to a rapid decrease in the quasiparticle scattering rate below $T_c$\cite{8, 27}. In this scenario the presence of defects in the films are again the likely explanation for the difference between films and crystals. This view is strongly supported by systematic studies of $R_s(T)$ in Zn-doped crystals where it was found that the presence of Zn impurities limited the decrease in the scattering rate, suppressed the broad peak in $R_s(T)$ and lowered the overall loss, giving a surface resistance very similar to that observed in the lowest loss thin films\cite{24, 25}.

The present article brings together the results of a systematic study of the effects of Zn and Ni doping on the surface resistance and penetration depth of YBa$_2$Cu$_3$O$_{6.95}$ crystals. These two impurities are currently under close scrutiny because they both substitute for Cu in the CuO$_2$ planes but have rather different effects on $T_c$ and other physical properties. In the experimental section, we will summarize the experimental techniques involved in our surface impedance measurements, including recent refinements that have improved both the precision and the absolute accuracy of the surface resistance and penetration depth measurements. The section on high purity crystals will focus on the surface impedance of undoped YBa$_2$Cu$_3$O$_{6.95}$ crystals, including recent measurements of the surface resistance of a twin-free
crystal. The results of Zn and Ni doping will be presented in the impurities section and at the end, the interpretation of these results in terms of both a generalized two-fluid model and calculations for a d-wave pairing state will be discussed.

**Experimental**

All of the measurements presented here have been obtained by cavity perturbation techniques using superconducting microwave resonators. When a small superconducting sample is inserted into a resonant cavity in a perturbation measurement, the small changes in the resonant frequency and $Q$ of the cavity provide the means of measuring $X_s(T)$ and $R_s(T)$. The change in $1/Q$ of the cavity provides a relatively straightforward measure of the surface resistance via

$$\Delta \frac{1}{Q} = \left[ \frac{1}{Q_s} - \frac{1}{Q_0} \right] \propto R_s$$

where $Q_0$ is the $Q$ of the empty cavity and $Q_s$ is the $Q$ of the cavity with the sample inserted. The relationship between the frequency shift and the surface reactance is complicated by the fact that the dominant effect of inserting a sample into a cavity is an overall shift of the resonant frequency by an amount proportional to $V_s/V_r$, where $V_s$ is the sample volume and $V_r$ is the effective volume of the resonator. The surface reactance is proportional to the penetration depth of the microwave fields and provides a relatively small frequency shift $\delta f \propto -\Delta V_s/V_r$, where $\Delta V_s$ is the volume of the sample penetrated by the microwave fields. $\delta f$ is the frequency shift relative to that which would be measured for a sample with perfect screening and no penetration of the microwave fields. The net frequency shift is

$$\frac{\Delta f}{f_0} = \frac{f_s - f_o}{f_0} \propto \frac{V_s}{V_r} \left[ 1 - \frac{\Delta V_s}{V_s} \right]$$

where $f_o$ and $f_s$ are the resonant frequencies of the unloaded and loaded cavity, respectively. In principle both $R_s(T)$ and $X_s(T)$ can be measured in the same cavity, but the measurement of $X_s(T)$ is complicated by the large geometric frequency shift, $V_s/V_r$. It is typically not possible to determine this shift, either by calculation or the use of reference samples, with sufficient accuracy to obtain reliable absolute values of $X_s(T)$. Instead, the change in
the reactance from its value at some base temperature \( T_0 \) is measured:

\[
\Delta X_s(T) = \mu_0 \omega \Delta \lambda(T) = \mu_0 \omega (\lambda(T) - \lambda(T_0)) \propto -[f_s(T) - f_s(T_0)]. \tag{3.6}
\]

Even with this compromise it is difficult to measure \( R_s(T) \) and \( \Delta \lambda(T) \) in the same cavity with sufficient precision to yield useful information over the full range from low temperature to the normal state of a high temperature superconductor. The central difficulty is that the measurements of very small \( R_s \) values in the superconducting state require careful measurement of \( Q_s \) and \( Q_0 \); thus, one must be able to move the sample in and out of the resonator to get a good measure of the small change in \( Q \). Precise measurements of \( \Delta X_s(T) \) have completely the opposite requirement. The sample must not be allowed to move during the course of the measurement or changes in the geometric shift, \( V_s/V_r \), can contaminate or completely dominate \( \Delta X_s(T) \). Our solution has been to design specialized resonators for these different measurements.

An early version of the resonator used to measure \( \Delta X_s(T) \) has been described elsewhere\[15\]. The resonator is a split-ring operating near 900 MHz and coated with a superconducting Pb:Sn alloy to give a \( Q \) of roughly \( 10^6 \). The requirements for measurements of \( \Delta \lambda(T) \) to better than 1 Å are stringent: the resonator frequency must be stable to better than 1 Hz over the course of a measurement. The sample is mounted on a sapphire plate that holds the crystal in the homogeneous, axial, microwave magnetic field in the central bore of the split-ring (\( \mathbf{H}_r \parallel \mathbf{c} \)). The rest of the sample holder is designed to minimize any motion of the sample as the temperature is changed: the sapphire plate is attached to a sapphire block where the sample heater and thermometer are located and the rest of the resonator assembly is at the temperature of the regulated 1.3 K He bath and the temperature gradient between the sapphire block and the bath is sustained by a quartz tube. The rigidity and very low thermal expansion of the quartz tube minimize any sample motion over the relevant temperature range, 1.3 to 100 K. A series of measurements with the sample at different positions (in the first version of the resonator) indicated that the magnetic field is homogeneous enough that motion of the sample in these fields is not a significant source of error. However, motion of the sapphire plate in the inhomogeneous electric fields is a more difficult problem. This source of systematic error has been further reduced in a new version of the resonator that has a rectangular rather than a square bore. The flatter shape allows the sample to be mounted farther away from the strong electric fields near the gap in the split-ring and also
improves the homogeneity of the electric fields in the region where the sample resides. The new apparatus is capable of resolving frequency shifts of a few tenths of a Hertz which, for a typical sample size, allows measurements of $\Delta \lambda(T)$ to a few tenths of 1 Angstrom.

The calibration of the resonator was done with measurements on a Pb:Sn alloy sample with a $T_c$ of 7.2 K. One can define a frequency shift, $\delta f$, and change in Q, $\delta(1/Q)$, for a loaded resonator relative to the frequency and Q of a sample that completely excludes the microwave fields. These quantities are actually measurable for the normal state of the Pb:Sn sample because the superconducting state is close to behaving like a perfect conductor with very low surface resistance and negligible penetration relative to the normal state skin depth. Hence, $\delta(1/Q(T)) = 1/Q(T) - 1/Q(1.3K)$ and $\delta f = f(T) - f(1.3K)$. For Pb:Sn in the normal state the classical skin effect should hold accurately at 900 MHz and both $\delta(1/Q)$ and $2\delta f/f$ should be proportional to the classical skin depth, which can be determined from the dc resistivity via $\delta_{cl} = (2\rho_{dc}/\mu_0 \omega)^{1/2}$. Indeed, $\delta(1/Q)$ tracks the temperature dependence of $\delta_{cl}$ very well, but thermal expansion of the sample causes $2\delta f/f$ to deviate somewhat. Corrections for the thermal expansion brought both quantities into agreement with $\delta_{cl}$, as is shown in Fig. 3.10. For the purpose of calibrating the frequency shift measurements we actually made use of the relationship $\delta(1/Q) = 2\delta f/f$ for a metallic slab in order to obtain $\delta f$ from the measurements of $\delta(1/Q)$ of the Pb:Sn sample. For our measurement geometry, the frequency shift associated with a metallic sample in the classical skin effect regime can be expressed as

$$\delta f = K_n A \delta_{cl}$$

where $A$ is the area of the slab-shaped sample. Thus, with measurements of $\delta(1/Q)$, the dc resistivity, and the area of the sample, one can use Eq. 3.7 to obtain the calibration constant, $K_n$. With this calibration the London penetration depth in the superconducting state can be obtained from

$$\Delta \lambda(T) = \frac{\delta f(T)}{2K_n A}.$$  

(3.8)

The difference in the propagation constant in the normal and superconducting states is responsible for the factor of two difference in the calibration constants that appear in Eqs 3.7 and 3.8. One small correction is made to the data before Eq. 3.8 is used to convert frequency shifts to penetration.
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Figure 3.10: A comparison of the classical skin depth (solid line) of a Pb:Sn reference sample and the $2\delta f/f$ (triangles) and $\delta(1/Q)$ (squares) measurements performed in the split-ring resonator used for the measurement of $\Delta\lambda(T)$. The skin depth is determined from dc resistivity measurements with the use of the classical skin effect expression, $\delta_{cl} = (2\rho_{dc}/\mu_0\omega)^{1/2}$. The agreement between all of these quantities indicates that the Pb:Sn alloy is in the classical skin effect regime and this is used to find the calibration constant connecting $\delta f$ and $\Delta\lambda$ in the superconducting state.
depths: there is a small temperature dependent frequency shift for the bare sapphire sample holder that is subtracted from the data set. This amounts to roughly a 20% correction for measurements below 7 K where the shift associated with $\Delta\lambda$ is small, typically about 12 Hz, and paramagnetic impurities in the sapphire give a noticeable temperature dependence of $-2$ Hz to the frequency shift measured for a bare piece of sapphire. At higher temperatures the frequency shift due to the sample completely dominates any temperature dependence associated with the sapphire.

Surface resistance measurements were made with two different resonators; a cylindrical cavity operated in the $TE_{011}$ mode at 34.8 GHz and a split-ring resonator near 4 GHz[30]. Both resonators were coated with Pb:Sn which gives a $Q_0$ of $2 \times 10^6$ for the split-ring and $1 \times 10^7$ for the cylindrical cavity. In both systems the sample is mounted on a sapphire rod which can be withdrawn for measurement of $Q_0$, and then reinserted into the axial magnetic fields of the cavity ($\vec{H}_r || \vec{c}$) such that currents are driven in the ab-plane of the crystal. The calibration constant that connects the $\Delta(1/Q)$ measured in this way with $R_s$ has been determined in two ways. At 34.8 GHz the skin depth in the normal state of YBa$_2$Cu$_3$O$_{6.95}$ is shallow enough that the classical skin effect formula can be applied directly to the measured surface resistance. Thus a measurement of the dc resistivity which gives $R_s$ in the normal state, and a measurement of $\Delta(1/Q)$ at the same temperature in the normal state can be used to obtain an internal calibration for each crystal. On the other hand, near 4 GHz the skin depth is comparable to the thickness of some of the crystals and this gives an enhanced $\Delta(1/Q)$ in the normal state that precludes using the previously described procedure. Instead, calibration is done by measuring $\Delta(1/Q)$ in the normal state of a Pb:Sn sample cut to the same size as the crystal. Measurements of crystals that are thick enough to use both calibration techniques give absolute values that agree to ±5%.

The Pb:Sn samples are also used to correct for small, non-perturbative effects in the resonators. The values of $\Delta(1/Q)$ for YBa$_2$Cu$_3$O$_{6.95}$ measured at low temperature are close to $10^{-7}$ in the cylindrical resonator and $10^{-8}$ in the split-ring resonator. At this level, non-perturbative contributions to $\Delta(1/Q)$ due to slight rearrangement of the microwave field pattern can be comparable to the contribution to $\Delta(1/Q)$ from actual loss in the sample. In order to measure the low temperature residual loss of the samples this extraneous contribution to $\Delta(1/Q)$ had to be measured and subtracted from the data. Measurement of the temperature dependence of $\Delta(1/Q)$ for several different
samples of Pb:Sn all show the rapid drop in loss expected for a conventional superconductor at low temperatures and then run into a sample-independent $\Delta(1/Q)$ by 2 K. Since it is unlikely that residual loss in the Pb:Sn samples would be the same from sample to sample, we attribute this limiting $\Delta(1/Q)$ to non-perturbative effects and subtract it from the $YBa_2Cu_3O_{6.95}$ data sets. At 3.88 GHz this correction amounts to $\Delta(1/Q) \sim 10^{-9}$, or a correction of roughly 7 $\mu\Omega$ in $R_s(T)$, about 10 % of the loss of a typical $YBa_2Cu_3O_{6.95}$ crystal at 40 K. At 34.8 GHz the correction is typically less than 5 % of the 40 K loss, or about 100 $\mu\Omega$.

Finally, a dominant limitation on the sensitivity of our earlier loss measurements with these superconducting resonators was the presence of microphonics. When the Q is very high, even a very slight vibration of the sample in a resonator’s fields leads to a modulation of the resonant frequency which limits the accuracy of the measurement of $\Delta(1/Q)$. Particularly for the split-ring resonator, a reduction of the microphonics has led to a significant improvement in the precision of the measurements.

**High Purity Crystals**

The measurements presented here of the surface impedance of crystals of $YBa_2Cu_3O_{6.95}$ are a continuation of studies already reported in the literature[8, 15, 27]. The crystals are grown by a flux-growth technique described in detail elsewhere[31]. Despite the fact that high purity starting materials are used, microwave measurements and elemental analysis by ICP mass spectroscopy both indicate that the crystals typically contain $\sim 0.1\%$ impurities. The most likely source of this contamination is impurities introduced into the melt as the flux corrodes the zirconia crucible. The crystals are very homogeneous, with $T_c$'s near 93.4 K and a transition width of only 0.25 K as seen in the specific heat jump, which provides a bulk measure of the transition.

**Penetration Depth**

Fig. 3.11 displays $\Delta\lambda(T) = \lambda(T) - \lambda(1.3\,\text{K})$ for two typical crystals. As has been discussed previously, the measurement geometry used here, with $\vec{H}_{rf} \perp \hat{c}$, involves currents running in the $\hat{c}$-direction as well as in the ab-plane[15]. Provided that $\lambda_{ab} \ll c$ and $\lambda_c \ll a, b$, the measured $\Delta\lambda$ in this geometry is given by $\Delta\lambda = a\Delta\lambda_{ab} + c\Delta\lambda_c$, where $a$ is the width of the crystal.
Figure 3.11: The low temperature behaviour of $\Delta \lambda(T) = \lambda(T) - \lambda(1.3\,\text{K})$ for two different crystals of YBa$_2$Cu$_3$O$_{6.95}$ is nearly linear between 5 and 25 K, with a small sample dependent curvature at the lowest temperatures.
Figure 3.12: The quantity $\lambda^2(0)/\lambda^2(T)$ gives the temperature dependence of the superfluid fraction $x_s(T)$. The linear asymptotic behaviour below 35 K is clear as well as a steep slope in the mean field regime near $T_c$. The values in this figure are derived from the data shown in Fig. 3.11 by assuming a value of 1400 Å for $\lambda(0)$. 
in the ab-plane and c is the thickness. Since $\lambda_c/\lambda_{ab} \sim 7$ the very thin samples $(a/c \sim 20)$ that we measure only involve contributions from $\lambda_c$ at the 10 to 15% level. Both data sets shown in Fig. 3.11 have a nearly linear temperature dependence between 5 and 25 K that is in good agreement with our earlier measurements[15]. Recent measurements on a similar crystal at 17 GHz with $\vec{H}_{rf} || \vec{c}$ are similar and have confirmed the linear temperature dependence in a geometry that measures only $\Delta \lambda_{ab}$[32]. The improved sensitivity of the measurements more clearly reveals a slight curvature below 5 K that we find to be somewhat sample dependent. Variation from sample to sample might arise from variation in defect concentration from crystal to crystal or from different $\lambda_c$ contributions due to different thicknesses.

Although $\Delta \lambda(T)$ is the quantity that is directly accessible by microwave measurements it is useful to construct the quantity $x_s(T) = \lambda^2(0)/\lambda^2(T)$ which is a measure of the superfluid fraction. This quantity can be generated by adding 3 $\AA$ to the data shown in Fig. 3.11 in order to take into account the fact that the measurements are relative to the value at 1.3 K rather than $T=0$ and then choosing a value of $\lambda(0)$. The resulting quantity shown in Fig. 3.12 has been generated with $\lambda(0) = 1400\AA$, close to the value suggested by far-infrared[33] and $\mu$SR[7] measurements performed on similar crystals. The superfluid density has a nearly linear temperature dependence between 5 K and 35 K with a slope, $dx_s/dt = -0.52$, where $t$ is the reduced temperature, $T/T_c$. The slope at $T_c$ is $-3.0$, 50% steeper than that of a weak-coupling BCS superconductor.

### Surface Resistance

Fig. 3.13 displays the surface resistance of a twin-free crystal measured at 4.13 and 34.8 GHz. The main qualitative features; the rapid drop at $T_c$, the broad peak near 40 K, and the rather weak temperature dependence below the peak, are all nearly the same as those observed in earlier measurements[25, 26]. However the improvements in measurement technique and the use of a twin-free sample have led to a few differences in detail. The minimum in $R_s(T)$ near 75 K is deeper in the twin-free crystal. We find that morphological defects such as growth steps and twin boundaries often cause some filling-in of this minimum, particularly in the lower frequency measurements. Also, the peak in $R_s(T)$ at 4.13 GHz is larger in amplitude and centered at a slightly lower temperature than it is in our previously published data[26]. Most importantly, the residual microwave loss at low temperatures...
is lower than that found in twinned crystals, less than 5 μΩ at 4.13 GHz and less than 150 μΩ at 34.8 GHz.

Although the surface impedance is the experimentally accessible quantity in microwave techniques, the complex conductivity, \( \sigma = \sigma_1 - i\sigma_2 \) (for the convention \( J \sim J_0 e^{i\omega t} \)), makes closer contact with the microscopic properties of the material. In MKS units the surface impedance is given by

\[
Z_s = R_s + iX_s = \left( \frac{i\mu_0\omega}{\sigma_1 - i\sigma_2} \right)^{\frac{1}{2}}.
\]  

(3.9)

for the case of local electrodynamics. Fortunately, the short mean free path, \( l \), in the normal state and the short coherence length, \( \xi_0 \), in the superconducting state guarantee that simple, local electrodynamics are adequate for calculating the properties of YBa\(_2\)Cu\(_3\)O\(_{6.95}\). Eq. 3.9 can be used to derive a general expression for determining \( \sigma_1 \):

\[
\sigma_1 = \sqrt{\left( \frac{\sigma_8}{2} \pm \sqrt{\frac{\sigma_8^2}{4} - \sigma_2^2} \right)^2 - \sigma_2^2}.
\]  

(3.10)

where the \( +(-) \) sign is used for the case \( \sigma_1 > (<) \sqrt{3}\sigma_2 \). \( \sigma_8 \) is a measurable quantity,

\[
\sigma_8 = \frac{\mu_0\omega}{2R_s^2}
\]  

(3.11)

that can be determined from surface resistance measurements and corresponds to the value of \( \sigma_1 \) in the case of a normal metal (where \( \sigma_1 \gg \sigma_2 \)) in the classical skin effect regime (local electrodynamics). Eq. 3.10 is useful in the superconducting state because \( \sigma_2 \) depends only on the London penetration depth at low frequencies. In the superconducting state the conductivity may be expressed as

\[
\sigma(\omega, T) = \sigma^*(\omega, T) - i\frac{1}{\mu_0\omega\lambda^2(T)}
\]  

(3.12)

where the second term is the screening response of the superfluid and the first term contains all other contributions to the conductivity. At low frequency (\( \omega\tau \ll 1 \), where \( \tau \) is the transport lifetime) \( \sigma^* \) has only a real part, \( \sigma_1 \), and penetration depth measurements can then be used to determine the imaginary part via \( \sigma_2 = (\mu_0\omega\lambda^2)^{-1} \). Thus, in the superconducting state we use Eq. 3.10 to extract \( \sigma_1 \) from measurements of \( R_s \) and \( \lambda \). In the
Figure 3.13: The ab-plane surface resistance of a twin-free crystal of YBa$_2$Cu$_3$O$_{6.95}$ measured at 4.13 and 34.8 GHz. The lack of twin boundaries has led to a lower residual loss than that typically observed in twinned crystals.
superconducting state, except for a small temperature range near $T_c$, $\sigma_1 \ll \sigma_2$ and Eq. 3.10 reduces to

$$\sigma_1(\omega, T) = \frac{2R_s(\omega, T)}{\mu_0^2 \omega^2(T) \lambda^2(T)}.$$  \hspace{1cm} (3.13)

Although we use Eq. 3.10 to analyze our data, Eq. 3.13 is much more transparent than Eq. 3.10 and is useful for understanding the factors that contribute to the measured surface resistance.

Fig. 3.14 displays the real part of the conductivity extracted from the penetration depth shown in Fig. 3.12 and the surface resistances shown in Fig. 3.13. The large, broad peak in $\sigma_1(T)$ is the feature responsible for the non-monotonic behaviour of $R_s(T)$ in the single crystals, although the temperature dependence of the screening term, $\omega^2 \lambda^2(T)$, makes the feature less pronounced in $R_s(T)$. Similar peaks have been observed in THz spectroscopy on films that continue the trend observed in the crystals: the peak diminishes and shifts to higher temperature with increasing frequency[34]. The peak in $\sigma_1(T)$ is quite different from the coherence peak of an s-wave BCS superconductor which rises abruptly just below $T_c$ and peaks at a higher temperature as well. Rather than being a coherence peak, broad peaks at low frequency in $\sigma_1(T)$ have been attributed to a rapid decrease below $T_c$ in the quasiparticle scattering rate[8, 27, 34, 35]. A very similar peak in the thermal conductivity has been explained in the same way[37], although the phonon contribution to the thermal conductivity complicates the interpretation of the thermal conductivity[38, 39]. The behaviour of the far infrared optical conductivity of Bi$_2$Sr$_2$CaCu$_2$O$_8$[36] and YBa$_2$Cu$_3$O$_{6.95}$[33] has also been interpreted in terms of a rapid decrease in the scattering rate below $T_c$.

The broad peak in $\sigma_1(T)$ can be understood, at least qualitatively, in the context of a two-fluid model of the low frequency conductivity. The real part of the conductivity can be divided into two terms[8, 40]:

$$\sigma_1(\omega, T) = \frac{ne^2}{m^*} \left[ x_s(T)\delta(0) + x_n(T)\frac{\tau(T)}{1 + \omega^2\tau^2(T)} \right].$$  \hspace{1cm} (3.14)

The first term is the superfluid response, which is responsible for the the zero resistance at dc and also gives rise to the London screening term that dominates $\sigma_2(\omega, T)$. Measurements of the London penetration depth provide a measure of this superfluid fraction via $x_s(T) = \lambda^2(0)/\lambda^2(T)$. The second term in Eq. 3.14 is the normal fluid response that is distributed over a range
Figure 3.14: The ab-plane conductivity of the twin-free crystal of YBa$_2$Cu$_3$O$_{6.95}$ extracted from the $R_\phi(T)$ and $\lambda(T)$ measurements shown in Figs 3.12 and 3.13. Below 40 K the large difference between the conductivities at 4.13 and 34.8 GHz is additional confirmation that $\tau(T)$ increases a hundred-fold by 40 K giving rise to relaxation effects when $\omega\tau(T) \sim 1$ at 34.8 GHz.
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of frequencies and is modelled here with a simple Drude response. A sum rule governs the total area under $\sigma_1(\omega)$ and therefore the total oscillator strength is shared between the superfluid fraction, $x_s(T)$, and the normal fluid fraction, $x_n(T)$. In the clean limit ($l \gg \xi_0$) all of the oscillator strength associated with the total free carrier density $n$ is apportioned between these two terms so that $x_s(T) + x_n(T) = 1$. This scenario is confirmed by far infrared measurements which show that virtually all of the free carrier conductivity seen in the normal state ultimately collapses into the superfluid screening term at low temperatures[41]. At intermediate temperatures, $x_n(T)$ decreases as $T$ drops below $T_c$ and $x_s(T)$ builds up. Thus a broad peak in $\sigma_1(T)$ can result from competition between this decrease in $x_n(T)$ and a rapid increase in $\tau(T)$. Estimates based on Eq. 3.14 indicate that in YBa$_2$Cu$_3$O$_{6.95}$, $\tau(T)$ increases nearly two orders of magnitude before running into a limit due to impurities, at which point the temperature dependence of $x_n(T)$ wins out and causes the conductivity to decrease with decreasing temperature.

The huge increase in $\tau(T)$ implied by the 4.13 GHz measurements indicates that for the 34.8 GHz measurements $\omega \tau(T)$ should be of order unity below 30 K. This brings relaxation effects into play in the higher frequency data where the denominator of the normal fluid term in Eq. 3.14 tends to diminish the size of the peak in $\sigma_1(T)$ and shift it to higher temperature. This observed difference between the 4.13 GHz and 34.8 GHz data is separate confirmation that the quasiparticle lifetime does increase dramatically below $T_c$. Above $T_c$, far infrared measurements indicate that $\omega \tau(T) \sim 1$ at $\sim 2400$ GHz[41], so the observation of relaxation effects at 34.8 GHz is consistent with an increase in $\tau(T)$ by two orders of magnitude. This interpretation is also consistent with the smaller peak in $\sigma_1(T)$ observed at THz frequencies[34].

Finally, the asymptotic behaviour of $\sigma_1(T)$ at the two measurement frequencies should be noted. At 34.8 GHz $\sigma_1(T)$ is quite linear below 30 K. Although somewhat noisier, the data at 4.13 GHz also varies linearly with temperature below 24 K. At both frequencies some sample–dependent curvature is often observed below 5 K, similar to the sample–dependent curvature observed in $\Delta \lambda(T)$ at low temperatures. The twin–free crystal has the most linear conductivity that we have observed, suggesting that any curvature in $\sigma_1(T)$ at low temperatures is probably due to defects, either impurities or twin–boundaries. The asymptotic behaviour of $\Delta \lambda(T)$ and $\sigma_1(T)$ will be discussed further in the last section, but it is at least worth noting here that none of these measurements have the exponentially activated behaviour...
expected for an s-wave BCS superconductor.

**Zinc and Nickel Impurities**

As was discussed in the introduction, the possibility that defects are responsible for much of the sample variation encountered in surface impedance measurements of YBa$_2$Cu$_3$O$_{7-\delta}$ was a prime motivation for studying the effects that deliberately introduced impurities have on the surface impedance of single crystals. The observed properties of the high purity crystals suggest two types of effects. First, one can study the effect that impurities have on the quasiparticle lifetime. If there is indeed a hundredfold increase in $\tau(T)$ in the clean crystals, then the deliberate addition of impurities should place a limit on this increase, resulting in a decrease in the amplitude of the peak in $\sigma_1(T)$ and elimination of the relaxation effects at 34.8 GHz. Second, the possibility that YBa$_2$Cu$_3$O$_{6.95}$ might be made gapless by the addition of a modest level of impurities makes measurement of $\Delta\lambda(T)$ in impurity-doped crystals imperative.

Zn and Ni have been found to preferentially substitute for the Cu(2) atoms in the YBa$_2$Cu$_3$O$_{7-\delta}$ crystal structure[42, 43]. Thus, they provide a well controlled means of specifically disturbing the CuO$_2$ planes that are the key element common to all of the highest $T_c$ superconductors. The rather different effects that Zn and Ni have on the most basic properties such as $T_c$ and the dc resistivity suggest that these dopants provide an important testing ground for models of high $T_c$ superconductors. Zn has been found to have a more drastic effect on $T_c$ than Ni. Susceptibility measurements of $T_c$ for our two batches of YBa$_2$(Cu$_{1-x}$Zn$_x$)$_3$O$_{6.95}$ with x=0.0015 and 0.0031 indicate that the suppression of $T_c$ with impurity content is $\partial T_c/\partial x \sim 1260$ which is in good agreement with the early study of doped crystals by Chien et al[44]. A batch of crystals with a Ni content of 0.0075 gave $\partial T_c/\partial x \sim 390$ which is in good agreement with a recent study of Ni-doped thin films[45] and indicates that Zn depresses $T_c$ roughly three times more rapidly than Ni does. On the other hand, Ni is found to increase the dc resistivity above $T_c$ as much, or more, than Zn[45]. That is, Ni provides at least as much scattering of the holes as Zn does, but has a much less drastic effect on $T_c$.

Fig. 3.15a shows the striking effect that Zn impurities have on the penetration depth. Addition of 0.31% Zn is sufficient to completely disrupt the linear temperature dependence, leaving a nearly quadratic $\Delta\lambda(T)$. The
0.15% impurity level exhibits intermediate behavior that has also been observed in the $H_{rf} \parallel c$ field configuration for a crystal from the same batch[32]. This result demonstrates the sensitivity of $\Delta \lambda(T)$ to impurities and strongly suggests that defects are responsible for the sample dependent, quadratic behavior that is commonly observed in thin films of YBa$_2$Cu$_3$O$_{7-\delta}$. The effect of Ni impurities is in striking contrast to the Zn results. Fig. 3.15b shows that a 0.75% Ni impurity level, more than twice the concentration of Zn required to completely alter the linear term, has almost no effect on $\Delta \lambda(T)$. To an even greater extent than the case of the suppression of $T_c$, the penetration depth measurements show that Ni impurities disturb the superconducting pairing state of YBa$_2$Cu$_3$O$_{6.95}$ much less than Zn impurities do.

Our initial studies of the effect of Zn impurities on the surface resistance of YBa$_2$Cu$_3$O$_{6.95}$ have been presented elsewhere and the only significant new feature of the results shown in Fig. 3.16 is that the residual loss at low temperature is somewhat lower. However, all of the results shown in Fig. 3.16 are for twinned crystals, including the high purity crystal. Twin-free Zn-doped crystals are not yet available, so we can only draw conclusions from the effect that impurities have on the temperature dependence of the loss. As is the case with the measurements of $\Delta \lambda(T)$ the measurements of $R_s(T)$ demonstrate that the microwave properties of YBa$_2$Cu$_3$O$_{6.95}$ are extremely sensitive to impurities. The range of surface resistances shown in Fig. 3.16 covers much of the range of sample-dependent behavior observed in the best thin films, suggesting that the surface resistance of thin films is strongly influenced by defects of some sort. As shown in Fig. 3.17, Ni impurities are also very effective at suppressing the broad peak in $R_s(T)$, both at 3.88 and 34.8 GHz.

As was done for the twin-free crystal in the previous section, the $R_s(T)$ and $\Delta \lambda(T)$ measurements can be used together to generate $\sigma_1(\omega, T)$ for the doped crystals. The only difficulty with this is that the dependence of $\lambda(0)$ on impurity content is not well known and a value of $\lambda(0)$ is needed to extract $\sigma_1(\omega, T)$ from the microwave measurements. However, at the rather low impurity concentrations studied here it is reasonable to use the 1400 Å value assumed for the pure crystals. Since it is expected that impurities will increase $\lambda(0)$, this assumption leads to an overestimate of the magnitude of $\sigma_1(\omega, T)$ for the impurity-doped crystals, but does not affect the overall shape of the curves. Figs 3.18a and 3.18b show the conductivity of the Zn and Ni-doped crystals, respectively, compared to a high purity crystal.
Figure 3.15: Comparison of the effect of Zn (a) and Ni (b) impurities on the temperature dependence of the London penetration depth. The sequence shown in (a) from pure (squares) through 0.15% (stars) to 0.31% (solid circles) substitution of Zn for Cu shows a change from linear temperature dependence to the quadratic behaviour expected for a gapless superconductor. On the other hand, (b) shows that 0.75% substitution of Ni impurities (solid triangles) has virtually no effect on the penetration depth.
Figure 3.16: Measurements of the surface resistance at 34.8 GHz demonstrate the strong influence that defects have on the microwave loss. The sequence from pure (solid squares) through 0.15% (stars) to 0.31% (solid circles) Zn substitution shows that the peak is suppressed and the overall loss is decreased by the addition of defects. The lowest curve is similar to that observed in the lowest loss films.
Both impurities suppress the amplitude of the peak in $\sigma_1(T)$ and shift it to somewhat higher temperatures. The coherence peak of an s-wave BCS superconductor that has a large, inelastic scattering rate should be little affected by the addition of the small level of impurities that we have used\cite{46,47}. Thus the suppression of the peak in $\sigma_1(T)$ that we observe for low levels of impurities in YBa$_2$Cu$_3$O$_{6.95}$ is further evidence that the peak is not due to coherence effects. Instead, the observed suppression of the peak shows that the presence of impurities places a limit on the rapid increase in $\tau(T)$, which in turn limits the rise in $\sigma_1(T)$ below $T_c$. A further indication that these low levels of impurities are limiting the large increase in $\tau(T)$ is the disappearance of relaxation effects in the crystal with Ni impurities. In the context of a two-fluid model (see Eq. 3.14) the large difference between the 3.88 and 34.8 GHz curves for the high purity crystal indicates that $\omega \tau \sim 1$ at 34.8 GHz and $\tau$ must have risen by two orders of magnitude below $T_c$. The addition of Ni then limits the increase in $\tau(T)$ enough that $\omega \tau \ll 1$ at 34.8 GHz and $\sigma_1(34.8 \text{ GHz, } T) \sim \sigma_1(3.88 \text{ GHz, } T)$.

A noteworthy difference between the effects of Zn and Ni impurities is apparent in Fig. 3.18. The low temperature behaviour of $\sigma_1(T)$ at 34.8 GHz for the Zn–doped series changes from the linear temperature dependence observed in the high purity crystal to a nearly quadratic temperature dependence at 0.31%; a progression that is similar to the effect of Zn on the low temperature behaviour of $\Delta \lambda(T)$. The Ni–doped sample shows no sign of this quadratic temperature dependence in either $\Delta \lambda(T)$ or $\sigma_1(T)$. Nickel and zinc have qualitatively different effects on the low temperature behaviour of both $\Delta \lambda(T)$ and $\sigma_1(\omega, T)$.

Models of the Surface Impedance

There are two key conclusions that can be drawn from the foregoing surface impedance measurements, independent of any models or microscopic theory. The first is that the impurity studies have rather solidly confirmed that a rapid increase in the quasiparticle lifetime below $T_c$ is responsible for the large peak in $\sigma_1(T)$ in YBa$_2$Cu$_3$O$_{6.95}$. The dependence of the amplitude of the peak on frequency and impurity content points to an increase in $\tau(T)$ by roughly two orders of magnitude between $T_c$ and 40 K. This conclusion can be made more quantitative by applying the generalized two-fluid model to extract $1/\tau(T)$ from the measurements of $R_s(T)$ and $\Delta \lambda(T)$. Eqns 3.10–3.12,
Figure 3.17: Substitution of 0.75% Ni impurities (triangles) is sufficient to lower the overall loss and completely suppress the broad peak observed in the pure sample (squares) even though $T_c$ is only decreased to 90.6 K.
Figure 3.18: The effect of Zn (a) and Ni (b) impurities on the conductivity. Both figures include the 3.88 GHz (open squares) and 34.8 GHz (solid squares) results for a high purity, twinned crystal. Fig. 3.18a shows that substitution with 0.15% (stars) and 0.31% (solid circles) Zn impurities suppress the peak in the 34.8 GHz conductivity and shift it to higher frequency. The suppression of the peak is the result of an impurity limit imposed on the rapid increase in $\tau(T)$, which results in a limit on the initial rise in $\sigma_1(T)$ below $T_c$. The Zn impurities also give rise to a quadratic temperature dependence in $\sigma_1(T)$ at low temperatures. Fig. 3.18b shows that 0.75% Ni substitution (3.88GHz, open triangles; 34.8 GHz, solid triangles) also suppresses the peak but does not generate the quadratic behaviour at low temperatures.
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...which are used to extract $\sigma_1(\omega, T)$ from $R_s(T)$ and $\Delta \lambda(T)$, are simply based on the electrodynamics of a local superconductor and the only significant assumption involved in extracting $\sigma_1(\omega, T)$ from our measurements is that a value for $\lambda(0)$ must be assumed in order to generate $\lambda(T)$ from $\Delta \lambda(T)$. Eq. 3.14 defines the generalized two fluid model that we use to try to interpret the data further. The division of oscillator strength between a normal fluid term with weight $x_n(T)$ and a superfluid term with weight $x_s(T)$ where $x_s(T) = \lambda^2(0)/\lambda^2(T)$ is based on the sum-rule that governs $\sigma_1(\omega)$ and the fact that it is the density of carriers in the superfluid term that is responsible for London screening at low frequencies. The weakest assumption of the model is the Drude form with a frequency-independent lifetime that we choose for the normal fluid spectrum. This is likely an oversimplification, but in YBa$_2$Cu$_3$O$_{6.95}$, the temperature dependence of the scattering time is such a large effect that a Drude spectral shape is sufficient for modelling the main effects observed at microwave frequencies.

Fig. 3.19 shows the scattering rate extracted from the measurements on the twin-free crystal. The small residual loss at low temperatures (5 $\mu\Omega$ at 4.13 GHz and 100 $\mu\Omega$ at 34.8 GHz) has been subtracted from the data sets before the analysis. The subtraction only has a significant effect on the inferred values of $1/\tau(T)$ below 10 K. Thus, insofar as the two-fluid analysis is valid, the values of $1/\tau(T)$ shown in Fig. 3.19 are reliable down to about 10 K. The two-fluid analysis of the 4.13 GHz data indicates that $1/\tau(T)$ falls by more than a factor of 100 from its value of $2.5 \times 10^{13}$ s$^{-1}$ just above $T_c$ to a value of about $1.4 \times 10^{11}$ s$^{-1}$ at low temperatures. This implies that at low temperatures $\omega \tau = 1.5$ at 34.8 GHz and places the low temperature 34.8 GHz data in the regime where relaxation effects are important. The fact that $\omega \tau$ is of order unity is consistent with the observation that the $\sigma_1(34.8$ GHz, $T) \sim \frac{1}{2} \sigma_1(4.13$ GHz, $T)$ below 30 K.

The quantitative differences between $1/\tau(T)$ inferred from the data at the two different frequencies indicate that the Drude spectral shape does not adequately model all of the details of the conductivity. In the temperature range above 50 K, $\omega \tau \ll 1$ at both frequencies and a Drude $\sigma_1(T)$ would be frequency-independent. Instead, we find that $\sigma_1(T)$ is 30 % larger at 4.13 GHz than it is at 34.8 GHz. This disagreement with the two-fluid model can be traced right back to the surface resistance where we find at high temperatures $R_s \propto \omega^{1.8}$ rather than the $\omega^2$ behavior expected from the two-fluid model at low frequencies. This weaker frequency dependence is close to that observed in conventional superconductors where the diverging density of...
Figure 3.19: The quasiparticle scattering rate inferred from the measurements of $\sigma_1(T)$ and $\Delta\lambda(T)$ for the twin-free crystal at 4.13 GHz (open squares) and 34.8 GHz (closed squares) shows a rapid decrease by a factor of 100 below $T_c$ as the holes condense in the superconducting state. The differences between these two curves are due to inadequacies in the Drude lineshape used to model the frequency dependence of the conductivity in the two-fluid model. The two fluid analysis also indicates that the addition of 0.31% Zn impurities (solid circles) increases the limit that $1/\tau(T)$ runs into. This impurity limit on $1/\tau$ is the source of the suppression of $R_s(T)$ in impure samples.
states at the gap edge leads to a logarithmic divergence in the frequency dependence of $\sigma_1$ at low frequency rather than the constant $\sigma_1$ of the two-fluid model. However, we have noted that the depth of the minimum in $R_a(T)$ is somewhat sample dependent and a small departure from $\omega^2$ behaviour in this temperature range may not be an intrinsic effect. At lower temperatures, where relaxation effects become important, the discrepancy in the $1/\tau$ inferred from the measurements at 4.13 and 34.8 GHz becomes quite large. This might be an indication of a frequency dependent scattering rate or it may also be a density of states effect. In an s-wave BCS superconductor, the effect of the diverging density of states gives conductivities near $\omega\tau \sim 1$ that differ substantially from those given by the Drude lineshape.[48] So, density of states effects, which require a more sophisticated model, might ultimately explain the finer details of $\sigma_1(\omega, T)$. Despite these limitations, the two-fluid model has appealing features. It provides a straightforward explanation of the peak in $\sigma_1(T)$ in terms of competition between $x_a(T)$ and $\tau(T)$ and it crudely accounts for the relaxation effects observed in the higher frequency measurements.

The results from applying the two-fluid model to the 34.8 GHz measurements of the 0.31 % Zn-doped sample are also included in Fig. 3.19. With the added impurity scattering, relaxation effects are not a problem, so the $1/\tau(T)$ at 34.8 GHz gives a reasonable measure of the effect of Zn on the scattering rate. The main result of the addition of the Zn impurities is an increase in the low temperature limit of the scattering rate. At 0.31% doping, $1/\tau(T)$ runs into an impurity limit of $1.4 \times 10^{12}$ s$^{-1}$. This impurity scattering can be compared to the results of Chien et al[44] who have studied the dc transport properties of Zn-doped crystals above $T_c$. Using a ratio of the carrier density to effective mass, $n/m^*$, that is set by our choice of $\lambda(0)$, the increase in dc resistivity that Chien et al observe corresponds to an increase in the scattering rate of $8 \times 10^{12}$ per atomic % substitution of Zn. So, the dc resistivity measurements indicate an increase in the scattering rate of $2.5 \times 10^{12}$ s$^{-1}$ for a 0.31 % Zn substitution, in reasonable agreement with the value that we infer from the microwave measurements below $T_c$. A two-fluid analysis of the conductivity of the 0.75% Ni-doped sample is rather uncertain because the residual loss is such a large fraction of the temperature dependent loss. Nevertheless, the nearly complete suppression of the peak in the conductivity indicates that the Ni doping provides at least as much additional scattering as the Zn impurities.

The second solid conclusion that can be drawn from the surface impedance
measurements is that there is a spectrum of excitations in the superconducting state that extends to very low energies in YBa$_2$Cu$_3$O$_{6.95}$. In particular, the lack of exponentially activated behaviour in either $R_s(T)$ or $\Delta\lambda(T)$ argues strongly against an $s$-wave BCS pairing state with a well developed gap in the excitation spectrum. A number of studies of possible pairing mechanisms in high $T_c$ superconductors have pointed towards the possibility of a pairing state with $d$-wave symmetry\cite{49, 50, 51}. Annett and Goldenfeld have shown that such a pairing state in the crystal symmetry appropriate for YBa$_2$Cu$_3$O$_{6.95}$ would have line nodes in the gap function that lead to a linear temperature dependence in $\Delta\lambda(T)$ at low temperatures\cite{12}. Given that a linear $\Delta\lambda(T)$ is in fact what we observe in our high quality crystals of YBa$_2$Cu$_3$O$_{6.95}$, the rest of the surface impedance measurements should be examined in the light of this possibility. There is already a significant body of calculations of electromagnetic properties of anisotropic pairing states; earlier work aimed primarily at the heavy fermion superconductors\cite{4, 21, 52}, and a more recent resurgence of interest in the context of high temperature superconductors \cite{12, 22, 53}. These studies include calculations of $\lambda(T)$, $\sigma_1(\omega, T)$, and the effects of impurities on superconductors with non-$s$-wave pairing states. In particular, recent calculations by Hirschfeld et al\cite{52} indicate that the linear behaviour of $\Delta\lambda(T)$ should be accompanied by a quadratic temperature dependence for $\sigma_1(T)$ at low frequency ($\omega\tau \ll 1$). That is, for our nominally pure, twin–free sample the region below 25 K that exhibits the linear $\Delta\lambda(T)$ should be accompanied by quadratic behaviour for $\sigma_1(T)$. Instead, we observe linear temperature dependence for $\sigma_1(T)$ at both 4.13 and 34.8 GHz in addition to the linear $\Delta\lambda(T)$. This concordance in the asymptotic behaviour of $\sigma_1(T)$ and $\Delta\lambda(T)$, shown in Fig. 3.20, is what one expects for a two–fluid model with a temperature–independent $\tau$ at low temperatures. Although the calculations of $\sigma_1(\omega, T)$ for a $d$–wave superconductor can be cast in the form of a two–fluid model, they contain a frequency and temperature-dependent $\tau$, even for impurity scattering. In particular, at low frequency and temperature, impurity scattering gives $\tau(T) \propto T$ which gives the extra power of $T$ difference between $\Delta\lambda(T)$ and $\sigma_1(T)$ in the $d$–wave calculations.

The doped samples provide further tests of the interpretation of the low temperature asymptotic behaviours. It has been well known that impurities, even non–magnetic ones, can make a superconductor with a non–$s$–wave pairing state gapless and that a distinctive feature of this gapless state is quadratic behaviour of $\Delta\lambda(T)$ at low temperatures\cite{21}. Hirschfeld and Gold-
enfeld have shown that a small concentration of impurities in a d-wave superconductor can lead to a crossover from $T^2$ behaviour at low temperatures to linear temperature dependence above some temperature, $T^*$[22]. Furthermore, for resonant scattering the quadratic low temperature regime should be in a measurable range for relatively small impurity concentrations that only have a small effect on $T_c$. The most obvious case for a crossover temperature is in the nominally pure samples which tend to show some curvature away from the linear temperature dependence below roughly 5 K. Similarly, Lee et al have reported crossover behaviour in thin films of YBa$_2$Cu$_3$O$_{7-\delta}$, though with a substantially higher crossover temperature of 25 K, presumably due to the higher level of defects in the thin films.[54] Fig. 3.21 displays the behaviour of the normal fluid density, $x_n(T) = 1 - \lambda^2(0)/\lambda^2(T)$ for the pure and Zn-doped samples, along with fits to an interpolation formula, $x_n(T) = aT^2/(T + T^*)$. These fits indicate that the crossover temperatures for the pure, 0.15 % Zn, and 0.31 % Zn samples are 3 K, 10 K, and 28 K, respectively. This sequence from the nominally pure sample with a low crossover temperature and predominantly linear temperature dependence, to a Zn-doped sample with a high crossover temperature and predominantly quadratic behaviour is in qualitative agreement with the theory of Hirschfeld and Goldenfeld[22]. Furthermore, the crossover temperatures are roughly those expected for resonant scatterers in a d-wave superconductor. For resonant scattering, $T^* \sim 0.83(\Gamma \Delta_0)^{1/2}$. The two-fluid analysis of the conductivity of the 0.31% Zn-doped sample indicated an impurity scattering rate of $\Gamma = 1/(2\tau) \sim 5$K. For an energy gap of $\Delta_0 = 3T_c$, this scattering rate gives $T^* = 31$K, quite close to the value inferred from the penetration depth measurements. This $T^*$ is high enough to almost completely eliminate the linear term in the penetration depth, leaving the quadratic behaviour associated with a gapless superconductor. The low temperature limit of the conductivity is also expected to be quadratic in the gapless regime, as is observed for the 0.31% Zn-doped sample at 34.8 GHz. Fig. 3.22 focusses in on the quadratic behaviour of both $x_n(T)$ and $\sigma_1(34.8\text{GHz}, T)$ for the 0.31 % Zn-doped sample at low temperatures.

Ni impurities do not fit into the same scheme of resonant scattering that seems to give a reasonable description of the Zn impurity effects. The 0.75 % Ni impurity level suppresses $T_c$ nearly as much as the 0.31 % Zn and provides at least as much scattering as the Zn impurities, but does not produce any quadratic, gapless behaviour in either $\Delta \lambda(T)$ or $\sigma_1(T)$. It is tempting to suggest that Ni might be a a non–resonant scatterer and that results for the
Born limit rather than the unitary limit are more appropriate. The $T^*$ for a Born scatterer is given approximately by $\Delta \theta e^{-\Delta \phi/\Gamma}$ which gives a much lower crossover temperature for a given scattering rate, $\Gamma$, than does the resonant scattering result. This could explain the persistence of the linear $\Delta \lambda(T)$ in the Ni-doped sample, but such a huge difference in the nature of the scattering for the two impurities bears closer examination.

conclusions

The striking qualitative features of the surface impedance of high purity crystals of YBa$_2$Cu$_3$O$_{6.95}$ lead to two far-reaching conclusions about the fundamental properties of this high T$_c$ superconductor. The broad peak in the surface resistance indicates that the quasiparticle scattering rate drops dramatically below T$_c$, falling from the large value caused by inelastic scattering above T$_c$ to a low value that is controlled by impurity scattering in the superconducting state. This phenomenon has manifested itself in far-infrared[36], THz spectroscopy[34], and thermal conductivity[37] measurements as well as the surface resistance and must be taken into account in the interpretation of any property in the superconducting state that is sensitive to the quasiparticle scattering rate. The fact that the inelastic scattering collapses as the holes condense in the superconducting state makes it clear that the large scattering rate in the normal state is primarily electronic in origin; there is neither a significant impurity nor a large phonon contribution to the scattering rate above T$_c$.

The linear temperature dependence observed for $\Delta \lambda(T)$ and $\sigma_1(T)$ at low temperatures indicates that there is a spectrum of excitations down to very low energies in the superconducting state. This linear behaviour is quite unlike the exponentially activated behaviour caused by the nodeless energy gap of a conventional s-wave BCS superconductor. Instead, the linear temperature dependence of $\Delta \lambda(T)$ is the asymptotic behaviour expected for a d-wave pairing state with line nodes in the energy gap. However, present calculations indicate that a d-wave pairing state with line nodes should have quadratic temperature dependence for $\sigma_1(T)$, rather than the linear behaviour that we observe for YBa$_2$Cu$_3$O$_{6.95}$. It is not yet clear whether this discrepancy is evidence against a d-wave pairing state or is the result of some assumption built into the theoretical calculations of $\sigma_1(\omega, T)$.

The fact that it has taken years to uncover these clear, qualitative fea-
Figure 3.20: The asymptotic behaviour of the conductivity at 4.13 GHz (open squares) and the normal fluid density (triangle). The linear behaviour of $\sigma_n(T)$ is consistent with a pairing state that has line nodes in the energy gap, but the linear behaviour of $\sigma_3(T)$ is at odds with the $T^2$ temperature dependence expected for the conductivity of a $d$-wave superconductor.
Figure 3.21: The low temperature behaviour of the normal fluid density, $\chi_n(T) = 1 - \lambda^2(0)/\lambda^2(T)$ in the nominally pure crystal (open squares) and the samples doped with 0.15% (stars) and 0.31% (solid circles) Zn. The solid lines are fits to an interpolation formula, $\chi_n(T) + aT^2/(T + T^*)$, which models the crossover from quadratic behavior at low temperatures to linear behaviour at higher temperatures. For the pure crystal the crossover temperature is low, $T^* \sim 3$K, but with the addition of 0.31% Zn, $T^* \sim 30$K and the linear regime is almost completely eliminated.
tures of the surface impedance of pure YBa$_2$Cu$_3$O$_{6.95}$ is a testament to the sensitivity of these properties to the presence of defects. This sensitivity has two sources. Most obviously, impurities control the size of the drop in the quasiparticle scattering rate below $T_c$ and the effect that this has on the microwave surface resistance is clearly demonstrated by the decrease in $R_s(T)$ with the addition of either Zn or Ni impurities. The second, more subtle, effect that impurities can have is to push YBa$_2$Cu$_3$O$_{6.95}$ into a gapless state. Addition of as little as 0.15% Zn impurities alters the linear behaviour of $\Delta \lambda(T)$ and 0.31% Zn makes both $\Delta \lambda(T)$ and $\sigma_1(T)$ quadratic; clear signs of gapless superconductivity. Further evidence for gapless superconductivity in Zn-doped YBa$_2$Cu$_3$O$_{7-\delta}$ includes a linear term in the electronic specific heat at low temperature that increases in magnitude as Zn is added$^{[55]}$ and NMR measurements that show Körnigka behaviour at low $T$ for $1/T_1$ when 1–2% Zn impurities are introduced$^{[56]}$. Although there is some controversy regarding the effect that Zn impurities have on the magnetic susceptibility$^{[57, 58]}$ the NMR results seem to indicate that the Zn ions are entering the lattice as a non–magnetic impurity$^{[56]}$. If this is indeed the case, the fact that we observe gapless behaviour for as little as 0.31% substitution of a non–magnetic impurity is in itself evidence for a pairing state other than the usual s–wave BCS pairing.

There is a further connection between the impurity studies presented here and the NMR results. Although the NMR measurements indicate that there is a local moment associated with Ni impurities, there is no sign of gapless behaviour in the NMR measurements of a sample containing 1% Ni impurities$^{[56]}$. Despite the fact that the Zn impurities are non–magnetic and the Ni impurities are magnetic, both the microwave and NMR measurements indicate that small levels of Zn impurities make YBa$_2$Cu$_3$O$_{7-\delta}$ gapless, but Ni impurities do not. This result is the opposite of that expected in an s–wave superconductor. Although the difference between these impurities might be attributed to a difference in their scattering strength, Zn being a resonant scatterer and Ni a Born scatterer, the NMR measurements suggest a situation that is rather complicated in detail. A key difference between Ni and Zn is that the Zn impurities alter the local spin fluctuations in the CuO$_2$ planes$^{[56]}$, a difference that has been suggested as an explanation for the stronger influence that Zn impurities have on the $T_c$$^{[59]}$. Taken altogether, the NMR and microwave measurements indicate a material with strong antiferromagnetic spin fluctuations and large inelastic scattering of charge carriers in the normal state and an unconventional pairing state con-
Figure 3.22: The asymptotic behaviour of the normal fluid density (triangles) and 34.8 GHz conductivity (squares) versus the square of the reduced temperature for the 0.31% Zn–doped sample. The quadratic temperature dependence of both quantities indicates that this low level of Zn impurities leads to gapless superconductivity in YBa$_2$Cu$_3$O$_{6.95}$. 
sistent with line nodes in the energy gap in the superconducting state. The striking difference between the effects of Ni and Zn impurities on all of these properties provides a rich basis for testing microscopic theories of both the normal state and superconductivity in YBa$_2$Cu$_3$O$_{7-\delta}$.

References


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3.3 Penetration Depth Measurements of 3D-XY Critical Behaviour in YBa$_2$Cu$_3$O$_{6.95}$ Crystals

Rather than exhibiting critical behaviour, the physical properties of bulk, classic superconductors near the superconducting transition temperature $T_c$ are generally well described by Ginzburg–Landau theory. Estimates of the Ginzburg temperature, $T_G$, at which Ginzburg-Landau theory is expected to break down, indicate that critical behaviour in classic superconductors is restricted to a temperature range that is inaccessibly close to $T_c$.[1, 2]. However, it has been recognised for some time that the small coherence length in the high temperature superconductors leads to the possibility of observing fluctuations and perhaps critical scaling near the superconducting transition.[1, 2, 3]. For a strongly type II superconductor, such as YBa$_2$Cu$_3$O$_{6.95}$, theory predicts[3] that the effective charge in the Ginzburg-Landau theory is negligible outside an inaccessibly small asymptotic regime close to $T_c$. Thus, for the purpose of understanding strong fluctuations in experimentally relevant temperature ranges, the order parameter may be regarded as neutral, and in the simplest case of a single complex order parameter would give rise to fluctuations in the universality class of the three dimensional (3D) XY model.

There has been considerable recent interest in the possibility of unconventional pairing states in the high-$T_c$ cuprate materials.[10]. Some of the possibilities under consideration involve order parameters corresponding to mixtures of irreducible representations of the symmetry group of the normal state, notably $s + id$ and $d + id''$, where $s$ and $d$ refer to order parameters with pure $s-$ or $d-$ like symmetry. Such states will either give rise to fluctuations in a universality class other than 3D XY near $T_c$ if the two representations are accidentally degenerate, or produce a second transition at a lower temperature. Since no second transition has been observed, observation of 3D XY critical behavior would suggest a single, complex order parameter.

Early measurements of transport and thermodynamic response in zero external magnetic field were interpreted in terms of Gaussian fluctuations about a mean field background.[4], although later analysis suggested the possibility of critical scaling in the universality class of the three dimensional (3D) XY model.[5]. More recent measurements in the presence of a magnetic field have also been interpreted as evidence for 3D XY critical scaling[6, 7, 8, 9]; in these measurements, the presence of a magnetic field effectively reduces
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the dimensionality of the system, with the result that the critical region is enlarged. In all of these works, the analysis of the data is invariably complicated by the necessity to perform a background subtraction, which is difficult to quantify reliably, in order to extract the fluctuation contribution.

In this article, we report microwave measurements of the $a-b$ plane electromagnetic penetration depth $\lambda(T)$ near the critical temperature of crystals of $YBa_2Cu_3O_{6.95}$. The penetration depth is a direct measure of the superfluid density $\rho_s \propto \lambda^{-2}$, which tends to zero as $T \to T_c$ in a manner determined by critical fluctuations. Thus, in contrast to the previous thermodynamic and transport studies[6, 7, 8, 9], no background subtraction is required to discern any fluctuation contributions to $\lambda(T)$.

The majority of microwave studies of surface resistance and $\lambda(T)$ have been performed on thin films[11], but the question of the role of defects in the electromagnetic properties of $YBa_2Cu_3O_{7-\delta}$ led us earlier to study high quality crystals[12]. Initial measurements were focused on the linear temperature dependence of $\lambda(T)$ found at low temperatures in nominally pure crystals, but it was also apparent that $\rho_s = \lambda^2(0)/\lambda^2(T)$ rises unusually rapidly below $T_c$[12]. In fact, we show in the present study that the measurements provide unambiguous evidence for critical fluctuations near $T_c$, consistent with the 3D XY universality class.

In our earlier studies, the influence of disorder on the low temperature behaviour of $\lambda(T)$ was examined by doping with Ni and Zn[13] in order to test a prediction based upon the hypothesis that the pairing state was $d-$wave[14]. Here we report that disorder is found to have little influence near $T_c$, consistent with the Harris criterion[1, 15], thus further strengthening the claim for critical behaviour. We emphasize that in this article, we only refer to the zero field scaling regime intermediate between mean field theory and the asymptotic scaling regime inaccessibly close to $T_c$, where fluctuations of the electromagnetic field must also be taken into account[16].

The $YBa_2Cu_3O_{6.95}$ crystals used in this study were prepared by a flux-growth technique described in detail elsewhere[17]. The sharpness of the specific heat jump at $T_c$, which provides a measure of the bulk homogeneity of a crystal, is an indicator of sample quality that has particular significance in studies of critical behaviour. A crystal produced by the technique used here exhibited a jump that was only 0.25 K wide (defined by the 10% to 90% points in the jump in $C_p/T$)[17], comparable to the narrowest transitions reported by Regan et al for a crystal of $YBa_2Cu_3O_{6.95}$[18] and by Buan et al for a twin–free crystal of $LuBa_2Cu_3O_{7-\delta}$[19].
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The experimental technique, a microwave technique discussed in detail elsewhere[12, 13], measures changes in the penetration depth with better than 1 Å resolution. The measurements involve cavity perturbation of a 900 MHz superconducting split–ring resonator with a thin plate–like crystal aligned so that $\vec{H}_{rf} \perp \vec{c}$. This geometry primarily measures the ab-plane penetration depth, $\lambda_\perp$, provided that the crystal is very thin. Placing a sample into a microwave cavity leads to a perturbation $\Delta \omega$ of the resonant angular frequency $\omega$ that can be expressed as

$$\frac{\Delta \omega}{\omega} = \frac{\Delta f}{f} - \frac{i}{2} \Delta \left(\frac{1}{Q}\right)$$

(3.15)

where $\Delta f$ is the shift in the resonant frequency $f$ and $\Delta(1/Q)$ is the change in the inverse of the quality factor of the cavity. For a slab of thickness $2c$ and infinite area, the perturbation in our measurement geometry is[12]

$$\frac{\Delta \omega}{\omega} = \frac{1}{2} \frac{V_s}{V_r} \left[1 - \tanh \frac{k c}{k c}\right]$$

(3.16)

where $k$, the propagation constant, is related to the complex conductivity, $\sigma = \sigma_1 + i\sigma_2$, by

$$k = (1 - i) \sqrt{\frac{\omega \mu_0 \sigma}{2}}.$$  

(3.17)

$V_s$ is the volume of the sample and $V_r$, the effective volume of the resonator, is determined by measuring a Pb:Sn alloy sample in the normal and superconducting states[13].

The first term in Eq. 3.16, $V_s/2V_r$, is the dominant geometric frequency shift associated with the displacement of microwave fields by the entire sample volume. In order to measure the temperature dependence of $\lambda(T)$ very precisely, we mount the sample rigidly inside the resonator and measure the temperature dependence of the perturbation relative to that for the sample at 1.3 K. This helps eliminate the problem of spurious frequency shifts due to sample motion altering the $V_s/2V_r$ term. In this case, the relevant expression for the perturbation is

$$\frac{\delta \omega}{\omega} = -\frac{1}{2} \frac{V_s}{V_r} \frac{\tanh k c}{k c}$$

(3.18)

where we use $\delta \omega$ rather than $\Delta \omega$ to denote the shift relative to that of a sample that perfectly screens out the microwave fields. In terms of our
measured quantities, this perturbation is given by

\[
\frac{\delta \omega}{\omega} = \left( \frac{\delta f}{f} - \frac{A \lambda(1.3 K)}{V_r} \right) - i \frac{1}{2} \delta \left( \frac{1}{Q} \right)
\]

where \( \delta f \) and \( \delta(1/Q) \) are the measured shifts relative to those at \( T=1.3 \) K. The term \( A \lambda(1.3 K)/V_r \) is a correction to account for the fact that the fields are not screened perfectly at 1.3 K; they penetrate a distance \( \lambda(1.3 K) \), close to the low temperature limit of the London penetration depth. There is no need to correct the \( Q \) measurement for the sample’s microwave losses at 1.3 K because at low temperature they are much too small at 900 MHz to be measurable in our cavity. Combining Eqs 3.18 and 3.19, yields

\[
\left( \frac{\delta f}{f} - \frac{A \lambda(1.3 K)}{V_r} \right) - i \frac{1}{2} \delta \left( \frac{1}{Q} \right) = -\frac{1}{2} \frac{V_e}{V_r} \left( \frac{\tanh(kc)}{kc} \right).
\]

Using the measured values of \( \delta f/f \) and \( \delta(1/Q) \) and an assumed value for \( \lambda(1.3 K) \), this equation can be solved numerically for \( k \) from which \( \sigma_1 \) and \( \sigma_2 \) can be easily extracted. For all of the data in the superconducting state shown here, \( \sigma_2 \gg \sigma_1 \), and the penetration depth is determined by \( \lambda = (\mu_0 \omega \sigma_2)^{-1/2} \). This relationship between \( \sigma_2 \) and \( \lambda \) is valid provided that measurements are made at a frequency low enough that \( \omega \tau \ll 1 \), where \( \tau \) is the relaxation time of thermally excited quasiparticles in the superconducting state. Near \( T_c \) this lifetime is roughly \( \tau \sim \hbar/2k_B T_c \), ensuring that \( \omega \tau \ll 1 \) at microwave frequencies. However, in the far-infrared this is not the case and strong temperature and frequency dependence of the relaxation time can influence the apparent behaviour of \( \lambda \) at high frequency[20].

Finally, we must choose a value for \( \lambda(1.3 K) \) in order to generate \( \lambda(T) \) from our measurements. Both far-infrared[20] and \( \mu \)SR[21] measurements on crystals similar to the ones used here place the low temperature penetration depth between 1350 and 1450 Å. We will adopt a value of 1400 Å in the following presentation of the microwave measurements; none of our results depend sensitively on the choice of \( \lambda(1.3 K) \).

Now we turn to a discussion of the data. In the inset of figure 3.23 is plotted the superfluid density \( (\lambda(0)/\lambda(T))^2 \) as a function of temperature \( T \) for nominally pure \( \text{YBa}_2\text{Cu}_3\text{O}_{6.95} \). The plot exhibits noticeable curvature near \( T_c \), whereas linear behaviour would have been expected if the penetration depth were to follow the Ginzburg-Landau behaviour \( \lambda(T)/\lambda(0) \propto t^{-1/2} \), with the reduced temperature being \( t \equiv (T_c - T)/T_c \). The main part of figure 3.23
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Figure 3.23: Inset: $(\lambda(0)/\lambda(T))^2$ versus $T$ for nominally pure YBa$_2$Cu$_3$O$_{6.95}$. Main figure: The same data, but $(\lambda(0)/\lambda(T))^3$ versus $T$. The value of $\lambda(0)$ was taken to be 1400Å.

shows the same data replotted with the vertical axis $(\lambda(0)/\lambda(T))^3$. The linear behaviour for about nine degrees below $T_c$ indicates that $\lambda(T)/\lambda(0) \propto t^{-y}$ with $y \approx 1/3$.

Fig. 3.24 shows $\lambda(t)$ versus $t$ on a log-log plot, using $T_c = 92.74$ K, the value of the critical temperature obtained by extrapolating the $t^{-1/3}$ behaviour shown in Fig. 3.23. Because of the slight breadth of the superconducting transition there is a small uncertainty, about $\pm 0.03$ K, in the appropriate choice of $T_c$.

This uncertainty only has a serious influence on the point near $t = 0.001$ in the log-log plot, leaving nearly two decades in $t$ over which power-law behaviour is unambiguously observed. A fit to the data shown in Fig. 3.24 yields power-law behaviour, $\lambda(t) = \lambda_{\perp} t^{-y}$ with $y = 0.33 \pm 0.01$. The uncertainty in the exponent represents the range of values obtained for the range of choices of $T_c$. This value of the exponent is consistent with the notion that the data are well-described by a 3D XY critical regime over a temper-
Figure 3.24: A log-log plot of $\lambda^{-1}(T)$ versus the reduced temperature, $t \equiv (T_c - T)/T_c$. With the critical temperature of 92.74 K used in this figure, power law behaviour $\lambda(T) = \lambda_{\perp 0} t^{-y}$ is observed over two decades in reduced temperature. The solid line is a fit to the data, yielding $\lambda_{\perp 0} = 1186\AA$ and an exponent $y = 0.33 \pm 0.01$ that is consistent with the critical behaviour expected for the 3D XY model.
Figure 3.25: $(\lambda(0)/\lambda(T))^3$ versus $T$ for YBa₂(Cu₁₋ₓZnx)₃O₆.₉₅ with $x=0$ (squares), 0.0015 (triangles), and 0.0031 (diamonds). The addition of Zn impurities does not appreciably affect the power law behaviour below $T_c$.

The temperature range of order $10$ K. This range agrees well with the range over which the electronic specific heat has been claimed to vary logarithmically with temperature[5, 18].

Figure 3.25 shows the effect of small concentrations of Zn impurities. The value of the exponent seems to be unchanged from that of the nominally pure sample and the temperature range over which the critical behaviour is observed changes little with impurity content. The observation that the exponent is not affected by the addition of low levels of impurities is consistent with the identification of this behaviour as a 3D XY critical regime; there, the heat capacity exponent is slightly negative, and thus the Harris criterion predicts that the critical behaviour is not affected by weak disorder[1, 15].

Finally, we mention two possible complications to the simple interpretation given here to the data. The first is the possibility of a crossover to two dimensional behavior. A rough criterion for the observation of three
dimensional, rather than two dimensional, behaviour is that the correlation length \( \xi_z \) in the \( c \)-direction, as defined in [3], be greater than half of the interlayer spacing. In the 3D XY critical regime the \( a-b \) plane correlation length and penetration depth for \( T \to T_c^- \) are given by \( \xi_L(t) = \xi_{L0} t^{-\nu} \) and \( \lambda_L(t) = \lambda_{L0} t^{-\nu/2} \), respectively, with \( \nu \approx 2/3 \). The coefficients are related by a universal amplitude ratio, which follows from two-scale-factor universality[3, 22]:

\[
\frac{\lambda_{L0}^2}{\xi_{L0}} = \frac{\gamma \Lambda_{T_c}}{\pi c_s}
\]

where \( \Lambda_{T_c} = 2 \times 10^8 \AA K/T_c \) and \( c_s \) is a universal constant that has been estimated to be 0.5[22]. \( \xi_z \) is related to \( \xi_L \) by \( \xi_z = \xi_L \) with an anisotropy parameter \( \gamma \approx 0.2 \) for \( YBa_2Cu_3O_{6.95} \). Thus, in the 3D XY critical regime \( \xi_z(t) \approx c_s \pi \lambda_L^2(t)/\Lambda_{T_c} \), which gives \( \xi_z = 4.8 \AA \) at \( t = 0.1 \) and \( 103 \AA \) at \( t = 0.001 \). If one assumes that the CuO\(_2\) bilayers are well coupled, then half the interlayer spacing is 5.9 \AA \ and the above estimate of \( \xi_z \) implies that the condition for three dimensional critical fluctuations is satisfied over the range from \( t = 0.001 \) to 0.1. There is in principle the possibility of a gradual crossover to 2D fluctuations at lower temperatures, although the fluctuation dominated regime may not extend that far.

The second possible complication is that of strong-coupling effects. Although strong-coupling can increase the slope of \( \lambda^2(0)/\lambda^2(T) \) near \( T_c \)[23], the qualitative mean field behaviour is retained; that is, \( \lambda^2(0)/\lambda^2(T) \) remains linear in \( t \). The curvature of the data near \( T_c \) shown in the inset of figure 3.23 is a qualitative deviation from both the weak-coupling BCS and strong-coupling mean field results.

In conclusion, we have presented unambiguous evidence for 3D XY critical scaling behaviour in a temperature interval of order 10 K below \( T_c \). This is the critical behaviour expected for a transition to a superconducting state with a single, complex order parameter such as pure s-wave or \( dxy \). The implications of our findings for the fluctuation contribution to the dc conductivity[24] will be presented elsewhere[25].

References

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3.4 Magnetic Penetration Depth and Surface Resistance in Ultrahigh Purity YBa$_2$Cu$_3$O$_{7-\delta}$ Crystals

Measurements of the electrodynamics of high temperature superconductors (HiTc) have played a crucial role in understanding the physics of these materials. The temperature dependence of magnetic penetration depth $\lambda(T)$ and microwave surface resistance $R_s(T)$ gives information about the nature of quasiparticle excitations, their dynamics and, indirectly, information on the structure of the gap function. However, many early attempts at measuring these quantities led to misleading conclusions, partly because of problems with sample quality. The first concern is purity: impurities can be introduced into the HiTc material either from the starting chemicals or from the crucible during crystal growth. The second concern is the quality of the surface. Since electrodynamic measurements involve probe currents that flow only within about a thousand angstroms of the surface of the crystal, it is natural to raise this concern, and one must distinguish between measurements probing the bulk, such as specific heat or thermal conductivity, and the ones probing the surface such as microwave or infra-red.

The linear temperature dependence of $\lambda(T)$ was first observed by Hardy et al. for YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) crystals grown in yttria stabilized zirconia (YSZ) crucibles (purity $\approx$ 99.9%) [1]. They found that $\Delta\lambda(T) = \lambda(T) - \lambda(1.2 K)$ below 20 K is largely linear with a slight, sample-dependent curvature below 4 or 5 K. Furthermore, studies of deliberate cation substitutions revealed that the penetration depth is very sensitive to certain type of impurities: for example, 0.3% Zn is enough to change the low temperature behaviour from linear to quadratic. Other types of crystal defects might have a similar effect; in particular, most films exhibit $T^2$ behaviour. It was therefore reasonable to believe that the observed sample variation in YSZ-grown pure crystals was due to the presence of impurities or other crystal imperfections.

Similar conclusions were drawn concerning the surface resistance of YBCO single crystals. Bonn et al. observed a peak in $R_s(T)$ of YSZ-grown crystals below $T_c$ which was attributed to a rapid increase in quasiparticle scattering time in the superconducting state[2]. However, the magnitude of the increase could be limited by deliberately introducing impurities: 0.3% Zn and 0.7% Ni were shown to be enough to completely suppress the peak. This left open the
question of whether or not the lifetime in YSZ-grown crystals is limited by the residual 0.1% impurities, or by some other mechanism. Like $\lambda(T)$, $R_s(T)$ also exhibits considerable sample dependence below 4 K. The magnitude of the residual $R_s(T)$ at 1.2 K varies considerably and the temperature dependence of $R_s(T)$ at low T varies from linear to quadratic in T [6]. These all point to the fact that the presence of residual impurities and crystal defects presents us from observing some important features of the intrinsic behaviour of $YBa_2Cu_3O_{7-\delta}$.

A breakthrough in improving the purity of YBCO crystals has been made through the use of $BaZrO_3$ crucibles instead of YSZ. Unlike YSZ, the $BaZrO_3$ crucibles are essentially inert and do not add measurable impurities to the melt during the growth process. This results in crystals with at least one order of magnitude increase in purity as well as higher crystallinity. Erb et al. were the first to grow such crystals[3] and Srikanth et al. have performed microwave measurements on them[4]. Recently Ruixing Liang in our group at UBC has succeeded in fabricating $BaZrO_3$ crucibles and growing high purity crystals in them. In this paper we present the results of our first series of measurements of the microwave surface impedance of this new generation of crystals.

The YBCO crystals are grown by a flux-growth technique in $BaZrO_3$ crucibles. Details of the fabrication of the crucibles and the crystal growth are given elsewhere[5]. The crystals have a purity of 99.99-99.995% and the width of the (006) rocking curve, which is a measure of crystal perfection, is $0.007^\circ$ (which includes $0.003^\circ$ instrumental resolution), a factor of 3 better than the YSZ grown crystals. The surface impedance measurements are performed using a superconducting loop gap resonator operating at 1.2 GHz. The sample is positioned inside the loop such that the RF magnetic field is applied parallel to the ab-plane of the crystal. This way the currents are mainly flowing in the ab-plane, with a small contribution from the the c-axis currents. In previous studies, we have separated out the c-axis contribution to $\lambda(T)[6]$ and most recently have done so for $R_s(T)$ [7]. However, in this paper we ignore c-axis contributions, which introduce errors of less than 5% to the results and will not affect qualitative features of the temperature dependencies.

In an attempt to determine optimal conditions for oxygen doping, we have measured $\Delta\lambda(T)$ for three crystals annealed in flowing oxygen at temperatures ranging from 450 to 500 °C. The areas of the crystals vary from 0.5 to 4 mm$^2$ and thicknesses vary from 25 to 55 microns. The data for all
Figure 3.26: $\Delta \lambda(T)$ vs $T$ for twinned crystals of $YBCO$ grown in $BaZrO_3$ crucibles with various annealing temperatures, 500 °C (circle), 475 °C (square) and 450 °C (star). Inset shows the variation of $T_c$ with annealing temperature.

three samples shown in Fig. 3.26 are similar, with no indication of the second order parameter component reported by Srikanth et al.[4]. The inset shows the variation of $T_c$ with annealing temperature, with the highest $T_c$ of 93.7 K achieved by annealing at 500 °C.

The same data, shown in detail below 20 K in Fig. 3.27, exhibits curvature which differs from the largely linear dependencies observed for $YSZ$-grown crystals. A likely explanation is that the chain oxygen vacancies are more mobile in the higher purity $BaZrO_3$ grown crystals and have a tendency to cluster. Erb et al.[8] have proposed that “fishtail”-shaped magnetization loops observed in their optimally doped crystals are in fact due to pinning by the vacancy clusters. From the point of view of microwave measurements, these clusters could act as electronic scattering centers, thus moving $\Delta \lambda(T)$ towards the quadratic temperature dependence observed in Zn-doped samples [2]. In the $YSZ$ grown crystals, impurities presumably impede the clustering process, so that the annealing conditions are less critical.

One obvious way to avoid clustering is to dope the crystals as close as possible to $O_7$, where it has been shown that the magnetization “fishtail” disappears [12]. Figures 3.28 and 3.29 show the results of this approach. The
crystals were detwinned and then annealed for 50 days, with the annealing temperature initially set at 450 °C and then decreased in several steps, the last one being 350 °C which corresponds to O\textsubscript{6.993}. Figure 3.28 shows $\Delta \lambda(T)$ and the superfluid fraction $n_s(T)$ for the a- and b-directions over the whole temperature range below $T_c \approx 88.7$ K. The $\Delta \lambda$'s are similar to those shown in figure 3.26 and do not differ substantially from data on crystals grown in YSZ crucibles. As yet, the zero temperature values of penetration depth, $\lambda(0)$, of these crystals are not known. We have used values $\lambda_a(0) = 1600$ Å and $\lambda_b(0) = 800$ Å which are inferred from $\mu$SR measurements for overdoped $YBCO$ crystals\[9\]. However, the choice of $\lambda(0)$ does not affect the qualitative features of the superfluid density, namely no signature of a second order parameter component developing below $T_c$ as reported by Srikanth \textit{et al.}, and non-mean field behaviour near $T_c$.

Fig. 3.29 shows the detailed behaviour of the data below 20 K, revealing a slight curvature in $\Delta \lambda$ in the a-direction and very linear temperature dependence in the b-direction. Linear fits to $\Delta \lambda(T)$ give a slope of 4.0 Å/K and 3.0 Å/K for the a- and b-directions respectively, which is very similar to the slopes of 4.0 Å/K and 3.2 Å/K observed for overdoped $YBCO$ crystals grown in YSZ crucibles. Power law fits to $n_s$ below 20 K give exponents of

![Figure 3.27: Same data as in figure 3.26 shown below 20 K.](image)
Figure 3.28: $\Delta \lambda(T)$ vs $T$ (right axis) and superfluid density $n_s$ vs $T$ (left axis) for a detwinned crystal of YBa$_2$Cu$_3$O$_{6.993}$, for a-(circle) and b-(square) directions.

1.06 and 0.94 for the a- and b-directions respectively, very close to linear.

We call attention to the fact that the linear temperature dependence persists down to the 1.15 K base temperature, whereas for YSZ-grown crystals we typically observe a cross-over towards higher power laws below 4 or 5 K. This supports the conjecture that the curvature observed in YSZ-grown crystals is due to the presence of the $\sim$0.1% impurities: the new crystals have more than an order of magnitude higher purity and correspondingly little curvature. Kosztin and Leggett[10] have predicted that non-local effects can result in deviations from the expected linear temperature dependencies even for a pure d-wave superconductor. However, as they have noted, non-local effects for the ab plane penetration depth are mainly important in the geometry where the magnetic field is applied parallel to the c-axis. In the measurements reported here, the RF field is applied parallel to the ab-plane and non-local effects should be negligible.

Previous measurements of $\lambda(T)$ in our laboratory have shown non-mean field behaviour close to $T_c$. Kamal et al. observed that in YSZ-grown crystals, the superfluid density shows the critical behaviour of the 3DXY universality class and that, surprisingly, the critical region is as wide as 10 K[11]. In figure 3.30 we show $\lambda^3(0)/\lambda^3(T)$ (circles) for a twinned $YBCO$
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Figure 3.29: Same as figure 3.28 but shown for below 20 K. All solid lines are linear fits to the data.

A single crystal grown under optimal doping conditions in a $\text{BaZrO}_3$ crucible. The crystal was annealed at 500 °C to an oxygen content of $O_{6.92}$ and has $T_c \approx 93.78$ K and most importantly, has a very sharp transition of less than 0.25 K wide. For $\lambda_0$ we have chosen 1400 Å, the same value used for twinned, $\text{YSZ}$-grown crystals, but again the results are not very sensitive to this value. As seen in the figure, this crystal also shows 3DXY critical fluctuations over a fairly wide temperature range, ~10 K, very similar to $\text{YSZ}$ grown crystals. The squares show a log-log plot of $\lambda$ as a function of reduced temperature, $t = 1 - T/T_c$, over more than 3 decades. The solid line is a fit to a power law $\lambda(t) = \lambda_1 t^{-y}$ with $y = 0.34 \pm 0.01$, where the error corresponds to assuming ±200 Å error in $\lambda(0)$.

The loop gap resonator and sample holder used in these measurements were designed mainly for precision measurements of $\lambda(T)$. However, we have recently succeeded in making simultaneous measurements of surface resistance using this resonator, thanks to recent improvements in the unloaded $Q$ ($Q_0 \approx 4 \times 10^6$) and to the use of time domain techniques. In our surface resistance measurements we are usually able to withdraw the sample from the resonator in order to find the unloaded $Q$. This is not possible in the present configuration and we can only measure the change of surface resistance, $\Delta R_s(T) = R_s(T) - R_s(1.15K)$. However, from other measurements
Figure 3.30: 3DXY critical behaviour of the super fluid density in the superconducting state of a sample annealed to \(YBa_2Cu_3O_{7-\delta}\). On comparable crystals we know that the residual \(R_s\) is very low, probably less than 2 \(\mu\Omega\).

Figure 3.31 shows \(R_s(T)\) for the a- and b-directions. The main features are similar to our previous results on crystals grown in \(YSZ\) crucibles, where the peak at 25 K is attributed to a rapid rise in the quasiparticle scattering time below \(T_c\). In particular, there is no indication whatsoever of a second order parameter developing below \(T_c\) as reported by Srikanth et al.[4]. Even with the inclusion of a somewhat uncertain residual surface resistance, one of the striking features of the data is the average rise in \(R_s\) from its minimum at about 70 K to its maximum at 25 K is roughly four fold compared to the two fold increase in crystals from \(YSZ\) crucibles. We interpret this as indicating that in the new crystals the quasiparticle scattering time rises to a much higher limiting value than in the \(YSZ\)-grown crystals, a consequence of the higher purity of the \(BaZrO_3\)-grown crystals. Another noteworthy difference is that \(R_s(T)\) varies linearly with temperature all the way down to 1.15 K, with slopes of 0.52 and 0.21 \(\mu\Omega/K\) for a- and b- directions respectively.

In summary we have presented \(\Delta \lambda(T)\) and \(R_s(T)\) for very high purity crystals of \(YBa_2Cu_3O_{7-\delta}\) grown in \(BaZrO_3\) crucibles. The results show no
Figure 3.31: Surface resistance vs T for a detwinned crystal of YBa$_2$Cu$_3$O$_{6.993}$, for a-(circle) and b-(square) directions.
evidence for two order parameter components. This is consistent with the fact that the specific heat of $BaZrO_3$-grown crystals produced by Erb et al. [12] exhibits a peak at $T_c$ that is identical in size and shape to those seen in high quality YSZ-grown crystals [13]. The specific heat data on the new crystals also shows no sign of a second superconducting phase transition. It is difficult to reconcile this bulk measurement on the $BaZrO_3$-crystals with the surface impedance data of Srikanth et al. [4] which shows a rather weak increase in the superfluid density near $T_c$ and a new feature at lower temperatures. This disagreement with a bulk measurement, coupled with the fact that we have observed no sign of a second phase in our surface impedance measurements, forces us to conclude that all of the new features reported by Srikanth et al. arise from some sort of problem with surface of the crystals that they have been studying.

References


3.5 Microwave Spectroscopy of Thermally Excited Quasiparticles in $\text{YBa}_2\text{Cu}_3\text{O}_6.99$

Introduction

Over the past few years measurements of electrodynamic properties at microwave frequencies have proven to be a fruitful technique for studying the superconducting state of the high temperature superconductors. A key strength of the technique is that measurements of the real and imaginary part of the surface impedance $Z_s(\omega, T)$ provide complementary information on two aspects of the superconducting state; the superfluid density and the low energy excitations out of the condensate.

Measurements of the imaginary part of the surface impedance $X_s(T)$ provide a direct measure of the penetration depth $\lambda(T)$, which is determined by the temperature dependence of the superfluid density. The widespread observation of a linear temperature dependence of $\lambda(T)$ at low $T$ in many of the superconducting cuprates [1, 2, 3, 4, 5] has been a key piece of evidence suggesting nodes in the energy gap in these materials. Near $T_c$ the temperature dependence of $\lambda(T)$ has provided evidence of 3DXY critical fluctuations over a wide temperature range in $\text{YBa}_2\text{Cu}_3\text{O}_7$ [6].

Measurements of the real part of the surface impedance $R_s(T)$, when combined with the measurements of $\lambda(T)$, can be used to determine the real part of the microwave conductivity $\sigma_1(T)$, which is essentially electromagnetic absorption by quasiparticles excited out of the condensate (either thermally excited quasiparticles or excitations created by the absorption of photons). Early measurements of $R_s(T)$ at a few GHz exhibited a broad peak below $T_c$, caused by a very large peak in $\sigma_1(T)$ at these low frequencies. This peak was also observed at THz frequencies by Nuss et al. [8], and was attributed to a competition between two temperature dependences; the overall decrease with temperature of the number of thermally excited quasiparticles competing with a rapid increase below $T_c$ of the transport scattering time of these quasiparticles. This rapid increase in scattering time has been interpreted as a collapse of the inelastic scattering processes responsible for the large normal state resistivity of the high temperature superconductors and is an effect that is observed in thermal conductivity measurements [9] as well as in other electromagnetic absorption measurements at microwave [2, 10, 11, 12, 13, 14, 15, 16], far infrared [17] and THz frequencies [8, 18, 19].
The rapid increase in quasiparticle scattering time is well established by these measurements and the very long quasiparticle mean free paths resulting from this have been corroborated further by the thermal Hall effect measurements of Krishana et al. [20]. However, obtaining a quantitative determination of the scattering time and the details of its temperature dependence has been hampered by the need to use models to interpret the existing microwave data. The problem has been that although the step from $R_s(T)$ and $\lambda(T)$ to the conductivity $\sigma_1(T)$ is a matter of straightforward superconductor electrodynamics when in the local limit, the extraction of a scattering time from $\sigma_1(T)$ suffered from a dependence on an assumed model for the shape of the quasiparticle conductivity spectrum $\sigma_1(\omega)$.

In this paper we present measurements at 5 microwave frequencies, giving enough spectroscopic detail over a wide enough frequency range to produce a rather complete picture of the evolution of $\sigma_1(\omega, T)$ in the superconducting state. These results support the early model based on an ansatz that the thermally excited quasiparticles have a Drude-shaped conductivity spectrum and now provide a much clearer measurement of the temperature dependence of the quasiparticle scattering rate below $T_c$. We find that this scattering rate becomes extremely small and appears to become essentially temperature independent below about 20 K. At higher temperatures the scattering rate increases rapidly, initially at least as fast as $T^4$. In the following section we will describe the techniques used to produce this information and in Section 3.5 we will present the results along with details of the extraction of the microwave conductivity from surface impedance measurements. In Section 3.5 the microwave conductivity spectra will be presented along with the results of fits that generate the temperature dependence of the quasiparticle scattering rate. In Section 3.5 we will point out some of the implications of these results and in particular compare them to the present literature on conductivity in a $d$-wave superconductor.

**Experimental Techniques**

The property being directly probed in a microwave measurement on a superconductor is the complex surface impedance $Z_s(T) = R_s(T) + iX_s(T)$. One simplifying feature of the high temperature superconductors is that the superfluid response falls in the limit of local electrodynamics, so that $R_s(T)$ and $X_s(T)$ are related to the complex conductivity $\sigma(\omega, T) = \sigma_1(\omega, T) - i\sigma_2(\omega, T)$
in a straightforward way. This simple limit arises from the very small coherence length in these materials, which guarantees that $\xi \ll \lambda$. A particularly simple regime of the local limit occurs when $\sigma_2 \gg \sigma_1$ below $T_c$ and at low frequency, in which case one obtains the relations

$$R_s(T) = \frac{e^2}{\pi^2} \omega^2 \lambda^3(T) \sigma_1(\omega, T)$$

$$X_s(T) = \mu_0 \omega \lambda(T)$$

A more detailed discussion of the electrodynamics and the extraction of $\sigma_1(\omega, T)$ from $Z_s(T)$ will be presented in Section 3.5, but the equations above are useful for quick estimates and for understanding the main features of the microwave properties of these superconductors.

The expression for $R_s(T)$ in Eq. 3.22 embodies what is most difficult about the microwave measurements. It contains both $\sigma_1$ and a term of the form $\omega^2 \lambda^3$, and physically can be interpreted as the microwave absorption processes ($\sigma_1$) occurring within the rather shallow depth into which the microwaves penetrate (hence the term $\omega^2 \lambda^3$). This screening length set by the superfluid makes $R_s$ extremely small below $T_c$, such that for small single crystals, one is forced to employ cavity perturbation in very high Q microwave resonators. This is most often achieved by the use of microwave cavities made from conventional superconductors cooled to low temperature. This fixed frequency type of measurement must be performed with several resonators if one is to build up a complete picture of the microwave conductivity spectrum $\sigma_1(\omega)$.

The data presented here involve measurements with 5 resonators spanning a 1 to 75 GHz range and utilizing a number of variations on the basic method of cavity perturbation. The common feature is that all of the measurements have been performed on the same sample, a thin plate of $YBa_2Cu_3O_{7-\delta}$ oriented such that the microwave magnetic field of each cavity lay in the plane of the plate ($\mathbf{H}_{rf} \parallel \mathbf{b}$). This geometry has the advantage that demagnetization factors are small, so the surface current distributions are fairly uniform and are similar in all of the measurements, making comparison from frequency to frequency quite reliable. The disadvantage is that although this geometry mainly measures the surface impedance for currents running across the crystal face in the $\hat{a}$ direction, there is some admixture of $\hat{c}$-axis surface impedance coming from currents running down the thin edge of the crystal. However, we have previously shown that these effects are small for a thin crystal, because the temperature dependences of $R_s(T)$ and $X_s(T)$ are quite
weak in the $\hat{c}$-direction, except near $T_c$[21, 22]. The absolute value of $R_s(T)$ for the $\hat{c}$-direction is also quite low [22].

The measurements at 1 GHz were performed in a loop-gap resonator initially designed for measurement of $\lambda(T)$ [1]. Like most of the resonators used in this study, the loop-gap is plated with a Pb:Sn alloy which is superconducting below 7 Kelvin and has very low microwave loss at 1.2 Kelvin. In the case of the 1GHz loop-gap, the cavity Q can be as high as $4 \times 10^6$ at low temperature. Another feature common to all of the measurements is that the sample is mounted on a thin sapphire plate with a tiny amount of silicone grease, with the thermometry and sample heater located at the other end of the sapphire plate, outside of, and thermally isolated from the resonator. In this way the resonator can be held fixed at the regulated $^4$He bath temperature while the sample temperature is varied. A unique feature of the 1 GHz loop-gap system is that the sample is held fixed in the resonator, with the sapphire plate and thermometry stage supported by a thin walled quartz tube which sustains the temperature gradient between the $^4$He bath and the sample. This means that the sample cannot be removed from the resonator during the measurements, but we find this restriction is necessary for the high precision measurements of $\lambda(T)$ which rely on the sample being held rigidly in a position that does not vary when the temperature is changed. Without this type of construction, motion of the sample and sapphire plate in the fields of the resonator can give rise to experimental artifacts. This is because $\lambda(T)$ is determined from very small changes in the resonator frequency as the sample temperature is changed. This technique gives highly precise and reliable temperature dependences relative to the base temperature, but is limited to measuring differences; $\Delta \lambda(T) = \lambda(T) - \lambda(1.2 \, K)$ and $\Delta R_s(T) = R_s(T) - R_s(1.2 \, K)$. The value of $R_s(1.2 \, K)$ at 1 GHz is estimated by comparing to separate experimental runs where the resonator is loaded with only the sapphire sample holder. The need to do this in two separate experimental runs gives the 1 GHz $R_s(T)$ measurements a relatively large uncertainty in the form of a temperature-independent background value ($\pm 0.7 \mu\Omega$), although the resolution of the temperature dependence is much better than this. We do not attempt to extract $\lambda(1.2 \, K)$ from the microwave measurements, but instead use values inferred from muon spin rotation measurements [23]. None of the analysis discussed in this paper depends sensitively on this choice of $\lambda(1.2 \, K)$.

The 2 GHz measurements have been performed in a Nb split-ring resonator that will be described in more detail elsewhere[24]. Measurements at
Chapter 3. Study of Microwave Electrodynamics in \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) Single Crystals

13.4, 22.7, and 75.3 GHz have been performed in the axial microwave magnetic fields of the \( TE_{011} \) modes of three right-circular cylindrical cavities. In all of the measurements other than those at 1 GHz, the sample can be easily moved in and out of the resonator. This freedom to move the sample makes it difficult to measure \( \lambda(T) \) at the higher frequencies, due to problems of controlling motion of the sample as the temperature is changed. However, the sample motion is much too slight to have any influence on the measurements of \( R_s(T) \). The ability to measure \( Q_0 \) by pulling the sample out rather than doing a separate experiment makes the background uncertainty in these measurements much less significant than it is in the 1 GHz data. The surface resistance is determined from \( R_s(T) \propto 1/Q_s - 1/Q_0 \) where \( Q_0 \) is the Q of the empty cavity and \( Q_s \) is the Q with the sample inserted. A small correction for other sources of loss must be made by measuring the sapphire holder and grease without the sample. Then the only remaining uncertainty in the background is the influence of non-perturbative effects, which we check by measuring a superconducting Pb:Sn sample at 1.2 K. With these corrections, the estimated uncertainty in the background is 0.7, 0.2, 10, 20, and 360 \( \mu \Omega \) for the 1.1, 2.2, 13.4, 22.7, and 75.3 GHz data respectively. The calibration of the absolute value of the surface resistance is obtained by measuring a Pb:Sn reference sample whose normal state surface resistance is governed by the classical skin effect. These calibrations, together with the statistical scatter in the data amount to a total uncertainty of \( \pm 10\% \) or less at each frequency.

The sample used for these measurements was a single crystal of \( \text{YBa}_2\text{Cu}_3\text{O}_{6.993} \) grown by a flux growth technique using \( \text{BaZrO}_3 \) crucibles\[25\]. The \( \text{BaZrO}_3 \), which does not corrode during crystal growth, yields crystals of much higher purity \[25, 26\] (better than 99.99\%) than those grown in more commonly used crucibles such as yttria-stabilized zirconia and alumina. The sample was detwinned at 250 C under uniaxial stress and then annealed at 350 C for 50 days to produce a sample with nearly filled chain oxygen sites. This gives a slightly lower \( T_c \) (88.7 K) than the maximum obtained near an oxygen concentration of 6.91 \[25\], but provides particularly defect-free samples without the oxygen vacancy clustering discovered by Erb et al. \[27\]. The dimensions of the sample were initially 2x1x0.02 mm\(^3\) for the 1 GHz measurements, which have been reported elsewhere \[28\]. Subsequent measurements in the other resonators were performed on smaller pieces cleaved from the original crystal, but measurements at 22.7 and 75.3 GHz were repeated on different pieces to ensure that the sample was uniform.
Experimental Results and Analysis

Fig. 3.32 shows the surface resistance of \( YBa_2Cu_3O_{6.993} \) for currents running in the \( \hat{a} \) direction. At all 5 of the frequencies shown in the figure, the rapid drop in \( R_s(T) \) below \( T_c \) is due to the onset of screening by the superfluid, with the overall magnitude of the drop depending strongly on frequency as expected from the term in \( R_s(T) \) that varies as \( \omega^2 \chi^3(T) \). For easier comparison of the different frequencies, it is convenient to plot the low loss data in the superconducting state as \( R_s/\omega^2 \) versus temperature, as shown in Fig. 3.33. One feature of these figures is that above 65 K the loss scales as \( \omega^2 \) to within \( \pm 8\% \), a scaling that is expected if the microwave \( \sigma_1(\omega) \) is frequency independent above 65 K. This agreement lies within the estimated uncertainty in background and calibration constants, and provides a check of the degree to which one can compare the measurements at different frequencies.

The broad peak in \( R_s(T) \) was originally attributed to a quasiparticle scattering time \( \tau \) that increases rapidly with decreasing temperature below \( T_c \) and competes with a density of these thermally excited quasiparticles that...
Figure 3.33: The same measurements of surface resistance as shown in Fig. 1, but with the behaviour below $T_c$ emphasized by dividing out a frequency-squared dependence associated with superfluid screening.

decreases with temperature [7]. For the early measurements near 2 GHz it was suggested that the quasiparticle scattering time reaches a limiting value near 30 K, possibly due to impurity scattering, at which point the quasiparticle density takes over and causes $R_s(T)$ to fall again with further decreases in temperature [29]. The speculation that impurities are involved in the turnover at 30 K was partly checked by studying samples doped with Ni and Zn [30]. These doping studies showed either a smaller peak shifted to higher temperature or no peak at all, consistent with the quasiparticle scattering rate running into an impurity limit at higher temperature, even when only 0.15% Zn was added to the sample. This sensitivity to such low levels of impurities raises a serious concern over these earlier crystals grown in yttria-stabilized zirconia crucibles, because during crystal growth the residual impurity level due to uptake of material from the corroding crucible reaches the 0.1% level. The results shown here on a new higher purity sample confirm the original speculation that it is this residual impurity scattering that limits
the increase in quasiparticle lifetime, even in quite pure crystals. The low frequency surface resistance of the new crystal rises a factor of four above the minimum near 70 K, higher than the factor of two or less observed in earlier measurements of samples at 2 and 4 GHz [29]. The changes are consistent with the new samples having lower impurity scattering and so reaching a higher quasiparticle scattering time limit at a lower temperature than was seen in the yttria-stabilized zirconia grown crystals.

The frequency dependence of the peak in $R_s(T)$ provides further evidence of the rapid increase in the quasiparticle lifetime. In much higher frequency measurements on thin films, Nuss et al. [8] were the first to observe a similar broad peak in the THz range that shifted up in temperature and decreased in size at higher frequencies. They pointed out that this could be accounted for by relaxation effects. If the quasiparticle lifetime increases sufficiently that $\omega \tau \geq 1$, then the sample enters a regime where $\sigma_1(T)$ falls as $\tau$ continues to increase. So for high frequency measurements the temperature at which $R_s(T)$ reaches its peak roughly indicates where $\omega \tau = 1$ at each measurement frequency. The fact that we observe these relaxation effects at 13 GHz indicates that the scattering time $\tau$ exceeds 10 ps in the new samples.

To better understand the data it is desirable to extract $\sigma_1(\omega, T)$ from these measurements of $R_s(\omega, T)$. At the lowest frequency of 1 GHz, where $\omega \tau \ll 1$ and we have simultaneous measurements of $R_s(T)$ and $\lambda(T)$, it is straightforward to extract $\sigma_1(T)$ with only an assumption that the electrodynamics are local. The 1 GHz measurements of $\lambda(T)$ used in this analysis are shown in Fig. 3.34, plotted as $1/\lambda^2(T)$. The screening by the superfluid follows the local London model if a superconductor is in the limit $\xi \ll \lambda$. Strictly speaking, this local limit is more complicated for the case of a superconductor with nodes in the energy gap because the coherence length is then $k$-dependent and becomes large in the node directions. However, the consequences of this type of non-locality for the electrodynamics would only be observable at low temperatures and the effect would be small in the measurement geometry used here [31]. A much more serious problem for the data analysis is that at the higher frequencies where $\omega \tau \geq 1$, the thermally excited quasiparticles also contribute to the screening of microwave fields and it is then incorrect to use the 1 GHz measurements of $\lambda(T)$ in order to extract $\sigma_1(T)$ from $R_s(T)$. Effectively, the penetration depth becomes frequency dependent, a phenomenon that has been observed directly in mm-wave measurements on particularly high quality thin films [16]. Ideally this problem can be solved by measuring both $R_s(T)$ and $X_s(T)$ at each measurement
Figure 3.34: The temperature dependence of the a axis penetration depth of YBa$_2$Cu$_3$O$_{6.95}$ plotted as $1/\lambda^2(T)$, which is a measure of the superfluid density via $n_s c^2/m^* = 1/(\mu_0 \lambda^2)$.

frequency, but we have done this only at 1 GHz, for reasons discussed in the previous section.

It is possible to work around the fact that we have measurements of both the real and imaginary part at only one frequency, as long as there is adequate information on the frequency dependence of the real part of the surface impedance. The problem is analogous to the one faced in far infrared spectroscopy of opaque samples, where the reflectance, but not the phase of the reflected light, is measured over a wide frequency range. Kramers-Kronig relations are the usual solution if only one of the optical constants is known, but is known over a wide frequency range. In principle, data at the five microwave frequencies presented here could be connected to far infrared measurements of reflectance in order to perform this analysis and extract $\sigma_1(\omega)$ and $\sigma_2(\omega)$. However, such an analysis is difficult because there still exists a substantial gap in the mm-wave frequency range between our highest frequency measurement and the lowest frequency far infrared measurements on crystals. Some data have been obtained in the mm-wave region using
techniques such as time domain THz measurements [8, 18, 19] and direct infrared absorption [32], but these have all been performed on films rather than untwinned single crystals. The quasiparticle scattering rate is typically much higher in films than it is in single crystals, so data taken on such different samples cannot be analyzed together in this way. An alternative to a Kramers-Kronig analysis is to fit the frequency dependent surface resistance to a model, but this is not a very satisfactory procedure if one only has data at five microwave frequencies and one doesn’t know the shape of the conductivity spectrum a priori. A further problem with both of these techniques is that the far infrared data is only available at a couple of temperatures below $T_c$, so they can not be used to do a complete analysis of the data presented here.

Our main approach to analyzing the surface resistance data is to use the $R_s(T)$ measurements at 1 GHz to arrive at an estimate of how much screening by the thermally excited quasiparticles must be included when extracting $\sigma_1(T)$ from $R_s(T)$ at higher frequencies. Although the procedure involves some assumptions about the model for the screening, we will show that the corrections are small enough that the effect of uncertainty in the choice of model does not significantly affect the conductivities that we extract in the analysis. We begin by writing down a general 2-fluid expression for the microwave conductivity that includes contributions to the real and imaginary part from both the superfluid and normal fluid (the conductivity due mainly to thermally excited quasiparticles),

\[
\sigma(\omega, T) = \sigma_{1S} - i\sigma_{2S} + \sigma_{1N} - i\sigma_{2N}
\]

where $\sigma_{1S}$ and $\sigma_{2S}$ are the real and imaginary parts of the superfluid conductivity and $\sigma_{1N}$ and $\sigma_{2N}$ are the real and imaginary parts of the normal fluid conductivity. The superfluid contribution consists of a delta-function at $\omega = 0$ with an oscillator strength given by the superfluid density divided by the effective mass ($n_s/m^*$), and an imaginary part that is the inductive response of the superfluid at nonzero frequencies. This superfluid response can be expressed in terms of the penetration depth using $n_s e^2/m^* = (\mu_0\lambda^2(T))^{-1}$, and away from $\omega = 0$ the delta-function can be neglected, leaving

\[
\sigma(\omega, T) = \sigma_{1N}(\omega, T) - i \left[ \sigma_{2N}(\omega, T) + \frac{1}{\mu_0\omega\lambda^2(T)} \right].
\]
Thus, in general the real part of the conductivity comes from the normal fluid. The imaginary part has contributions from both the normal and superfluid, although the superfluid dominates at low frequency.

In the local limit the connection between $\sigma_1(\omega, T)$ and the surface impedance is made via

$$Z_s = R_s + iX_s = \left( -\frac{i\mu_0\omega}{\sigma_1 - i\sigma_2} \right)^{\frac{1}{2}}.$$ (3.25)

Thus, at 1 GHz where we have measurements of both $R_s$ and $X_s$, $\sigma_1$ and $\sigma_2$ can be extracted using

$$\sigma_1 = 2\mu_0\omega \frac{R_sX_s}{(R_s^2 + X_s^2)^2}$$ (3.26)

$$\sigma_2 = \mu_0\omega \frac{X_s^2 - R_s^2}{(R_s^2 + X_s^2)^2}.$$

At higher frequencies, where we only have measurements of $R_s(T)$, it is useful to write $\sigma_1$ in terms of $R_s$ and $\sigma_2$ in the following way [29]:

$$\sigma_1 = \left[ \frac{\sigma_s}{2} \pm \left( \frac{\sigma_s^2}{4} - \sigma_2 \sigma_s \right)^{1/2} \right]^{1/2} - \sigma_2^{1/2}$$ (3.27)

with the sign choice $+$ ($-$) for $\sigma_1 > (<) \sqrt{3}\sigma_2$

and where $\sigma_s = \frac{\mu_0\omega}{2R_s^2}$

In the normal state, where $\sigma_1 \gg \sigma_2$ at low frequencies, this expression reduces to the classical skin effect result $\sigma_1 = \mu_0\omega/2R_s^2$. Eq. 3.27 continues to be valid right through the superconducting transition and can be used to extract $\sigma_1$ from measurements of $R_s$ provided that one also has some information on $\sigma_2$. The extent to which one can use this expression in the superconducting state depends upon the relative importance of the normal fluid contribution to $\sigma_2$. In regimes where this contribution is small, $\sigma_2$ is simply given by $\sigma_{2S} = (\mu_0\omega\lambda^2(T))^{-1}$ which can be calculated from the penetration depth measurements. To clearly illustrate the problem that occurs when the normal fluid contribution to $\sigma_2$ is not small, we examine a particular version of the 2-fluid model where the normal fluid conductivity is assumed to have a Drude frequency dependence:

$$\sigma_{1N} - i\sigma_{2N} = \frac{n_ne^2}{m^*} \left[ \frac{\tau}{1 + (\omega\tau)^2} - i\frac{\omega\tau^2}{1 + (\omega\tau)^2} \right]$$ (3.28)
where \( \tau \) is the scattering time of the normal fluid and \( n_n/m^* \) is the normal fluid density over the effective mass. The ratio of the normal fluid and superfluid contributions to the effective screening is then

\[
\frac{\sigma_{2N}}{\sigma_{2S}} = \frac{n_n}{n_s} \frac{(\omega \tau)^2}{1 + (\omega \tau)^2}.
\] (3.29)

The normal fluid contribution to screening is thus unimportant at low frequency (\( \omega \tau \ll 1 \)) or when the normal fluid density is small (\( n_n/n_s \ll 1 \), which occurs at low temperatures). Conversely, difficulties arise when \( \omega \tau > 1 \) and \( n_n/n_s \) is not small, which is likely the case for our data at 13 and 22 GHz in the temperature range from 20–40 K, and for the 75 GHz data from 20–60 K.

For the conductivities that we will show below we take the following approach to estimating the normal fluid contribution to \( \sigma_2 \). At 1 GHz \( \sigma_1 \) is calculated directly from the simultaneous measurements of \( R_s(T) \) and \( X_s(T) \). Then we extract an estimate of \( \tau(T) \) using the Drude model above (Eq. 3.28). The normal fluid density is calculated from the penetration depth measurements by assuming that

\[
\frac{n_ne^2}{m^*}(T) + \frac{n_se^2}{m^*}(T) = \frac{n_se^2}{m^*}(T = 0).
\] (3.30)

which amounts to assuming that all of the low frequency oscillator strength is being shifted from the normal fluid to the superfluid as the temperature is decreased. The \( \tau(T) \) and \( n_n(T) \) derived from the 1 GHz data can then be used to make an estimate of the normal fluid contribution to \( \sigma_2 \) needed to analyze the data at higher frequencies. When this analysis is performed, we find that the normal fluid screening influences the extraction of \( \sigma_1 \) from \( R_s(T) \) only at the level of 20% or less. This can be understood if one notices that \( \omega \tau \sim 1 \) at temperatures of 50 K or less at which point the normal fluid density has already fallen below 20% of the total oscillator strength. There is some uncertainty associated with assuming a Drude form for \( \sigma_1(\omega) \) (Eq. 3.28) and assuming the redistribution of oscillator strength implied by the two fluid model (Eq. 3.30). However, we will show that for temperatures up to 45 K, deviations from a Drude spectrum are barely discernible within our experimental uncertainties and the two fluid model is obeyed at microwave frequencies to within 10%. Thus, the maximum systematic error that might be introduced by this analysis amounts to 3% at worst at 75 GHz, only
Figure 3.35: The temperature dependence of the $\hat{a}$-axis microwave conductivity of $YBa_2Cu_3O_{6.93}$ extracted from the surface resistance measurements of Fig. 1. The sharp spike near $T_c$ is a result of superconducting fluctuations and the broad peak at lower temperatures is caused by the increase in the scattering time of thermally excited quasiparticles.

about 1% at 13 and 27 GHz, and is completely negligible at 1 and 2 GHz. Furthermore, the values of $\tau(T)$ that we use in the analysis above turn out to be consistent with the conductivity spectra $\sigma_1(\omega)$ that will be discussed below, so the correction for screening by the normal fluid is self-consistent.

Fig. 3.35 shows the conductivities extracted from the $R_s(T)$ data of Fig. 3.32, using the methods described above. The sharp upturn at $T_c$ marks the presence of superconducting fluctuations, which have been discussed in greater detail by Kamal et al. [6] and Anlage et al. [33] and are not the main focus of the work presented here. A number of previous measurements on earlier generations of $YBa_2Cu_3O_{7-\delta}$ crystals have shown the presence of an extra sample-dependent peak in $\sigma_1(T)$ just below $T_c$, a feature that was discussed by Olson and Koch [34] and by Glass and Hall [35] who attributed it to having a sample with a broadened transition. A similar feature was also
Chapter 3. Study of Microwave Electrodynamics in YBa$_2$Cu$_3$O$_{7-\delta}$ Single Crystals

reported recently by Srikanth et al. for BaZrO$_3$-grown crystals [36], but since we see no sign of this in our new high purity samples, we conclude that such features are associated with a spread in $T'_c$ in the surface of the sample. The main feature that we do observe in the conductivity is that $\sigma_1(T)$ has a large broad peak, rising to nearly 25 times the normal state conductivity. The peak rises a factor of two higher than was seen in measurements at 2 and 4 GHz on an earlier generation of crystals grown in yttria-stabilized zirconia crucibles [30] and it crests at a lower temperature, 25 K instead of the 35 K turnover observed in the lower purity crystals. This effect of very low levels of impurities is not consistent with the suggestion of Klein et al. [37] that this feature is the result of BCS-type coherence effects. A coherence peak, essentially a density of states effect, is observed near $T_c$ in $\sigma_1(T)$ of s-wave superconductors such as Pb[38]. However, the peak observed here at 1 GHz is much too large and too low in temperature to be attributed to such an effect. Furthermore, a strong coherence peak has not been seen in NMR measurements of $T_1$ in this material [39] nor is it expected in a d-wave superconductor, the now widely accepted pairing state of $YBa_2Cu_3O_{7-\delta}$.

[40, 41]

Thus, in the absence of strong coherence effects, we have attributed the rise in $\sigma_1(T)$ below $T_c$ to a rapid increase in the scattering time $\tau$ of thermally excited quasiparticles, as discussed in the Introduction. The fact that this peak rises higher and turns over at a lower temperature in the new, higher purity crystals is consistent with this interpretation. That is, in the higher purity sample, $\tau$ runs into its impurity limit at a somewhat lower temperature than it did in the earlier generations of crystals and this impurity-limited scattering time is very large in the new BaZrO$_3$-grown crystals. An estimate of the increase can be made as follows. The penetration depth measurements indicate that more than 90% of the normal fluid density is gone at 25 K (see Fig. 3.34), so the 25-fold increase in $\sigma_1$ between $T_c$ and 30 K implies an increase in $\tau$ by at least a factor of 250 over the scattering time just above $T_c$. This is actually an underestimate because not all of the far infrared oscillator strength in the normal state ends up condensed into the superfluid at low temperatures. Such a huge increase in lifetime is consistent with the relaxation effects observed in the data at 13 GHz and higher. As a rough illustration of this agreement, far infrared measurements indicate that $\omega\tau \sim 1$ at about 3000 GHz just above $T_c$, so a 300-fold increase in $\tau$ below $T_c$ would mean $\omega\tau \sim 1$ at about 10 GHz, leading to the considerable frequency dependence in $\sigma_1(\omega)$ that we observe in the microwave range.
Figure 3.36: The conductivity spectrum at 4 selected temperatures between 4 and 20 K, extracted from the $\sigma_1(T)$ curves of Fig. 4. In this temperature regime, the conductivity due to thermally excited quasiparticles has a nearly temperature independent width of 8 GHz and a nearly temperature independent shape that is close to a Drude lineshape (the lines are Drude fits).

**Conductivity Spectra and Quasiparticle Lifetime**

The evolution of the conductivity with temperature is better illustrated in Figs. 3.36 and 3.37 where we show the conductivity spectrum $\sigma_1(\omega)$ at several representative temperatures. In fact, the central technical achievement of this work is that we now have measurements at enough frequencies that both the shape of $\sigma_1(\omega)$ and its temperature dependence are quite clear. Fig. 3.36 shows the conductivity spectrum at three temperatures below 25 K, the temperature range where we have argued above that the conductivity is dominated by thermally excited quasiparticles scattered by a low level of impurities. We will not concentrate here on the lowest temperature data, where the loss becomes very small and difficult to measure accurately by
Figure 3.37: The conductivity spectrum at 3 selected temperatures above 20 K, extracted from the $\sigma_1(T)$ curves of Fig. 4. Above 20 K, the width of the conductivity peak broadens rapidly, stretching out of the microwave frequency range above 55 K. These conductivity spectra continue to be reasonably well fit by Drude lineshapes, as shown by the lines in the figure.

most cavity perturbation techniques. Fig. 3.36 shows that from 4 to 20 K, the conductivity consists of a very narrow peak whose width is largely temperature independent. The lines in the figure are weighted, least squares fits to a Lorentzian lineshape (the real part of Eq. 3.28), demonstrating that the conductivity spectrum of the thermally excited quasiparticles is Drude-like. The main contributions to the error bars in these spectra are a combination of uncertainty in the individual measurements' calibration constants, plus a substantial uncertainty in the background loss in the 1.1 GHz measurements, and scatter in the 2.2 GHz measurements. Within these error estimates (mostly systematic error) there is very little clear deviation from a Drude lineshape when examining an individual spectrum at a particular temperature. The most noticeable deviation is in the spectrum at 4 K, where the data may be taking on a slightly more cusp-like shape than the Drude
Figure 3.38: A comparison of the normal fluid oscillator strength determined in two ways; from Drude fits to spectra like those of Figs. 5 and 6 and from the disappearance of oscillator strength in the superfluid response, as measured by $1/\lambda^2$ (Fig. 3).

The nearly Lorentzian lineshape largely confirms the ansatz originally used by Bonn et al. [29] to analyze the early $R_s(T)$ measurements.

An interesting cross-check of these fits to $\sigma_1(\omega)$ is to compare the oscillator strength in the normal fluid conductivity peak, which is given by the fit parameter $n_ne^2/m^*$, to the superfluid density $n_se^2/m^* = (\mu_0\lambda^2)^{-1}$ extracted from the penetration depth measurements. If one assumes that all of the oscillator strength ends up in the superfluid $\delta$-function as $T \to 0$, then the superfluid density is related to the normal fluid density via Equation 3.30. Fig. 3.38 shows a comparison between the normal fluid density inferred from the fits to the $\sigma_1(\omega)$ peaks and the normal fluid density inferred from the penetration depth via Eq. 3.30. This figure indicates that the normal fluid density does nearly track the decline of the superfluid density with increasing temperature, which indicates that our use of a two-fluid model to describe the screening is a reasonable procedure. The increasingly serious deviation between the curves above 40 K is an indication that the Drude lineshapes
do not completely keep track of where all of the oscillator strength is going as temperature increases. There is also some deviation at low temperatures, taking the form of a normal fluid oscillator strength that is extrapolating linearly towards a non-zero value as T→0. This is an indication of the presence of residual conductivity in the low temperature, low frequency limit, which is expected for a d-wave superconductor [42].

The quality of the fits to $\sigma_1(\omega)$ and the agreement in the oscillator strengths shown in Fig. 3.38 indicate that the Drude fits do provide a reasonable measure of the width of the peaks from 4 to 45 K. The temperature dependent width coming from these fits, which we interpret as the scattering rate of the thermally excited quasiparticles, is shown in Fig. 3.39. One of the key results of these measurements is that the width of the normal fluid peak is very small, 9±1 GHz, and it is nearly temperature-independent up to 20 K. The main change in the spectra in this temperature range is an increase in oscillator strength, due to the shift of spectral weight from the superfluid response (a $\delta$-function at $\omega=0$) to the microwave conductivity. The narrow width suggests a very long quasiparticle scattering time of $1.8(\pm0.2) \times 10^{-11}$ s.

One sees in Fig. 3.37 that above 25 K the conductivity peak broadens rapidly and by 60 K the width becomes much greater than the frequency range of the microwave measurements, so we have no direct measure of the width and shape of $\sigma_1(\omega)$ above 60 K. The exceptionally low level of defects in the new BaZrO$_3$ grown crystals, coupled with the measurements at 5 microwave frequencies, allows us to determine the temperature dependence of the inelastic scattering rate over a fairly wide temperature range from 20 to 40 K. Qualitatively similar results have been obtained in measurements on thin films by high frequency microwave and THz techniques [8, 19]. However, the much higher level of defects in such samples limits the temperature range over which the evolution of the inelastic scattering rate can be observed. In the high purity crystals, the temperature dependent scattering can be tracked all the way down to 20 K. A fit to the form $1/\tau(T) = A + B(T/T_c)^y$ from 4 to 40 K yields an exponent $y = 4.2 \pm 0.1$, with coefficients $A = 5.2(\pm0.4) \times 10^{10}$ s$^{-1}$ and $B = 4.6(\pm0.9) \times 10^{12}$ s$^{-1}$, and is shown as the solid curve in Fig. 3.39. The uncertainty in the exponent indicates the maximum range that is consistent with the data to within the estimated errors shown in Fig. 3.39.
Figure 3.39: The scattering rate of the thermally excited quasiparticles, as inferred from the width of Drude fits to the conductivity spectra of Figs. 5 and 6. The solid curve is a fit to a scattering rate that increases as $T^{4.2}$.

Discussion

For the purposes of discussing the data, we have divided the conductivity spectra up into the two regimes discussed in the previous section. In the range below about 20 K where the width of the peak in $\sigma_1(\omega)$ is narrow and nearly temperature independent, studies of samples over a wide range of purities indicate that this regime is governed by thermally excited quasiparticles being scattered by impurities or other defects [30, 50]. Waldram et al. have pointed out the possibility that non-local effects might come into play in the conductivity in this regime, leading to an effective scattering rate that is not influenced by the density of residual impurities [43]. However, the considerable narrowing of $\sigma_1(\omega)$ that we have observed upon going from YSZ-grown crystals to the higher purity $\text{BaZrO}_3$-grown crystals indicates that the samples are still in a regime where impurities play a role in the low frequency scattering. We have previously suggested an intuitively appealing
way to interpret the spectra in this regime, based on a specific version of the
two fluid model [29]. In this phenomenological picture, the quasiparticles
excited near the nodes in the energy gap have a temperature-independent
scattering rate due to elastic scattering by impurities and a conductivity
spectrum with a Drude lineshape whose width is set by this scattering rate
$1/\tau_i$ just like impurity scattering in a normal metal. In the high purity sam­

dles this $1/\tau_i$ would correspond to a strikingly long mean free path of $4 \mu m$
if one takes the Fermi velocity to be $v_F = 2 \times 10^7 cm/s$. In this particu­
lar two fluid model, the only source of temperature dependence in the low
temperature microwave conductivity is the density of the thermally excited
quasiparticles, which increases linearly with temperature. This is a straight­
forward consequence of the linear dispersion of the gap function near the
nodes and is also intimately connected to the linear temperature dependence
of the penetration depth (they are Kramers-Kronig related).

Parameterizing the normal fluid response in this way, with a tempera­
ture dependent density and a scattering rate, has been partly justified by
calculations of the microwave conductivity of a $d_{x^2-y^2}$ superconductor [44].
However, it is not so obvious that a temperature independent scattering rate
is expected for impurity scattering of these thermally excited quasiparticles
near the nodes, since they differ greatly from free carriers at an ungapped
Fermi surface. In particular, it has been pointed out by Hirschfeld et al.
that elastic impurity scattering in this situation should lead to a frequency
and temperature dependent scattering rate because of the restricted phase
space into which the quasiparticles at the nodes can scatter [44, 46]. So,
with this possible conflict between theory and the phenomenological model
in mind, we will make some more detailed comparison between the microwave
conductivity data and the relevant theoretical calculations.

The transport properties (both microwave conductivity and thermal con­
ductivity) of a $d_{x^2-y^2}$ superconductor have been the subject of considerable
theoretical effort recently [42, 44, 45, 46, 47, 48]. This work builds on ear­
lier calculations of the transport properties of anisotropic superconductors,
aimed primarily at explaining and predicting the properties of heavy fermion
superconductors [51, 52]. The high temperature superconductors now of­
fer an opportunity to test these calculations in a situation where we have a
relatively simple anisotropic pairing state. Such comparisons are somewhat
complex because the question of transport properties at low temperatures is
inherently a question of understanding impurity effects. This is especially
the case for anisotropic superconductors because the presence of impurities
has a strong impact on the excitation spectrum near gap nodes, particularly in the limit of unitary scattering.

A key effect of impurities in an anisotropic superconductor is to produce a band of impurity states with a width $\gamma$, thus giving the superconductor a non-zero density of states at the Fermi level. One surprising consequence of these states is a universal conductivity limit at low frequency as $T \to 0$, first pointed out by P.A. Lee [42]. This residual conductivity is independent of impurity concentration, the result of a cancelation between the density of states induced by the presence of the impurities and the lifetime associated with those states. A version of this universal limit has been observed by Taillefer et al. in thermal conductivity measurements of pure and Zn-doped $YBa_2Cu_3O_6.9$ below 1 Kelvin [53]. To the best of our knowledge, this limit has not yet been definitively observed in microwave conductivity measurements, in part due to sensitivity problems in the type of cavity perturbation measurement being discussed in this article. Instead, our main concern here will be the behaviour of this conductivity as temperature and frequency are increased, which involves conductivities that are substantially larger than the $T\to0$ limit and are thus easily measurable with the methods discussed above. This microwave conductivity has been the subject of considerable theoretical effort, including both numerical work and analytical results in certain limits [44, 45, 46, 47, 48].

One well studied case involves the electrodynamic properties at temperatures and frequencies below the impurity bandwidth $\gamma$, in the unitary scattering limit (scattering phase shift $\to \pi/2$). In this limit the impurity bandwidth is given roughly by $\gamma \sim (\Gamma\Delta)^{1/2}$ where $\Delta$ is the magnitude of the gap and $\Gamma$ is the elastic scattering rate that the impurities would contribute to the normal state resistivity. For $\omega, T < \gamma$, where the transport properties are dominated by this impurity band, it has been shown that both $\sigma_1$ and $\lambda$ vary as $T^2$ [44, 45]. This quadratic behaviour has been seen in Zn-doped samples of $YBa_2Cu_3O_{6.95}$, where it was found that at a Zn impurity concentration as low as 0.15 % the crossover energy scale is already $\gamma > 4 \text{ K}$ [49, 30]. However, Zn substitution for planar Cu’s is the only impurity that we have found that clearly gives this unitary scattering behaviour. Ni substitution for Cu, Ca substitution for Y, and the chain oxygen vacancies all have much weaker effects, even at defect levels of 1% or more [21]. The previous generation of YSZ-grown crystals showed only slight curvature in $\lambda(T)$ and $\sigma_1(T)$ below 4 Kelvin and the new $BaZrO_3$-grown crystals show no hint of $T^2$ temperature dependence down to 1.2 Kelvin. The relative rarity of $T^2$ behaviour
(though it is common in films for reasons that remain unclear [54]) leads us to consider the opposite limit for the strength of the scattering, the Born limit.

For impurity scattering in the Born limit, the crossover energy scale is exponentially small, so one does not expect to see the universal conductivity limit until measurements are performed well below 1 Kelvin. In fact, in the microwave measurements presented here we are also not necessarily at low enough frequency to observe any simple limiting behaviour. So, we compare our results qualitatively to numerical calculations performed in the Born limit by Hirschfeld et al. [46]. They found that at very low frequency $\sigma_1(T)$ rises rapidly from the universal zero temperature limit to a much larger conductivity that depends upon the impurity scattering rate. It remains fairly temperature independent until inelastic scattering processes become important. At higher frequencies $\sigma_1(T)$ becomes smaller and moves through a whole range of behaviours, varying from mostly sub-linear in $T$ at low frequency, through a quasi-linear temperature dependence at intermediate frequencies, to a faster than linear temperature dependence at high frequencies. Figure 3.40 shows behaviour in the measured microwave conductivity that is similar to this Born limit result in some of its qualitative features. The overall conductivity has a magnitude that varies with purity, from the quite high values seen here, through to very low, flat conductivities observed in Ni-doped samples [30]. More importantly, here we do clearly see for the first time that the linear behaviour of $\sigma_1(T)$ is an intermediate behaviour, albeit one that survives over a substantial range of frequency and temperature. The evolution in the shape of $\sigma_1(T)$ at low $T$ clearly falls outside of our phenomenological model, which would have predicted a linear temperature dependence at all of the frequencies shown in Fig. 3.40. That is, if $\sigma_1(\omega)$ were really Drude-shaped with a temperature independent width, then $\sigma_1(T)$ would exhibit the same temperature dependence at all frequencies; namely, the linear temperature dependence of the normal fluid density.

At our lowest frequencies the data does move towards sub-linear as expected in the Born limit. However, one perhaps important difference from the theoretical calculations is that the trend does not to continue below 2 GHz. The data stops evolving towards the expected low frequency behaviour, which is a rapid leap upwards to a constant value. The reason for this is not yet clear, so we are left for the moment with qualitative features that seem only weakly in accord with Born limit scattering. Other features of the data echo the expectations of a conductivity spectrum with a Drude-like lineshape.
Figure 3.40: This detailed view of the temperature dependence of the microwave conductivity below 20 K shows a gradual evolution of the shape of $\sigma_1(T)$, from concave up at high frequencies to concave down at the lowest frequencies. The quite linear temperature dependence seen here at 13 GHz seems to be an intermediate behaviour.
that has a temperature independent width; namely, the similarity in the 1 and 2 GHz curves and the relatively large frequency and temperature range over which \( \sigma_1(T) \) is nearly linear in \( T \). It is the latter aspects of the data that lead to the Drude model being a fairly good description of the conductivity spectra.

Although the foregoing discussion indicates that the \( \sigma_1(\omega) \) spectra cannot be perfectly Drude shaped, there is still a characteristic width to the peaks that is well parameterized by the Drude fits. Thus, the plot of scattering rates shown in Fig. 3.39 provides a reasonable measure of the narrowness of the peak at low temperature and its rapid broadening above 20 K. Just above 20 K, the initial onset of this increase in scattering appears to be at least as rapid as \( T^4 \) and must rise even more quickly at higher temperatures in order to meet the width observed in the normal state far infrared measurements. A rapid temperature dependence of the quasiparticle scattering time would be expected in any situation where the inelastic scattering comes from interactions that become gapped below \( T_c \). A number of early calculations tackled the problem of the collapse of the scattering rate below \( T_c \) in this way. Early on, Nuss et al. explained the peak in their THz conductivity measurements in this manner [8]. Littlewood and Varma studied this type of effect in a marginal Fermi liquid [55], the idea being that below \( T_c \) a gap opens up in the scattering spectrum. Statt and Griffin similarly studied the effect of the opening of a gap in the spectrum of spin fluctuations [56]. All of this work predated the solid identification of the \( d_{x^2-y^2} \) pairing state, so isotropic s-wave gaps were assumed in the calculations. Quinlan et al. studied a model in which quasiparticle lifetimes were associated with spin fluctuation scattering. They studied the effects of both s-wave and d-wave gaps opening up in the spin fluctuation spectrum [57]. Since we now know that the gap in this material has \( d_{x^2-y^2} \) symmetry, this latter calculation is most directly relevant to our measurements here. In particular they found that at temperatures well below \( T_c \), the quasiparticle lifetime increases as \( T^3 \) and even faster than this as \( T_c \) is approached. In a comparable temperature range, the transport scattering rate that we extract from the width of \( \sigma_1(\omega) \) is closer to \( T^4 \). Thus, the temperature dependence of the inelastic scattering rate seems to be about one power of \( T \) faster than the lifetime calculations based on a gapping of the spin fluctuation spectrum. One must note, however, that the quasiparticle lifetime can in principle differ from the electronic transport scattering time, since charge transport is most strongly affected by backscattering.
Conclusions

We have presented here the most complete microwave measurements yet obtained on a crystal of a high temperature superconductor. These spectra reveal a wealth of detail regarding the conductivity spectrum $\sigma_1(\omega)$ of the thermally excited quasiparticles in the superconducting state. We find that $\sigma_1(\omega)$ has a Drude-like shape. Although in detail there may be deviations from this shape, there is nevertheless a well defined characteristic width which can be associated with the transport scattering time of the quasiparticles. Below $T_c$, the width collapses rapidly and it becomes easily discernible in the microwave spectral range at temperatures below 55 K. In the range between 45 K and 20 K we find that the collapse of the scattering rate varies at least as fast as $T^4$. By 20 K the width becomes extremely narrow and nearly temperature independent. This narrow width of only 9 GHz corresponds to a mean free path as high as 4 $\mu$m if we interpret the width as being a direct measure of the elastic scattering rate due to impurities. We find that some features of $\sigma_1(\omega,T)$ below 20 K are in accord with quasiparticle scattering in the Born limit for a $d_{x^2-y^2}$ superconductor, in particular, a gradual evolution of the shape of $\sigma_1(T)$ from sublinear $T$ dependence at low $\omega$, to quasilinear and then faster at higher $\omega$. However, there remain discrepancies that might best be settled by a detailed numerical calculation aimed at fitting the observations presented here. Such fits must come to grips with the observation that the behaviour of $\sigma_1(\omega,T)$ below 20 K is reasonably well described by a model involving quasiparticle scattering with a temperature-independent scattering rate.

References


Chapter 3. Study of Microwave Electrodynamics in YBa$_2$Cu$_3$O$_{7-\delta}$ Single Crystals


Chapter 4

Summary of Thesis Contributions

In this thesis, a number of contributions to the knowledge and understanding of the electrodynamics of the HiTc cuprates have been made. Here, I will first summarize the highlights of the results obtained on the single crystals of YBa$_2$Cu$_3$O$_{7-\delta}$ grown at UBC. Then, I will review the contributions made to the development of the experimental setup which enabled us to perform measurements of magnetic penetration depth and surface resistance at 1 GHz with high precision.

4.1 Electrodynamics of HiTc Superconductors

The starting point for my project was on the measurements of magnetic penetration depth of high purity optimally doped YBCO single crystals grown in yttria stabilized zirconia crucibles. These measurements confirmed the earlier results obtained by Dr. Walter Hardy on the linearity of penetration depth below 20 K. Slight curvature observed at lower temperatures below about 4 K was attributed to the effect of impurities on a superconducting state with an unconventional order parameter. Furthermore it had been theoretically shown that the contrast between the effect of impurities with strong and weak scattering could distinguish between different order parameter symmetries which can produce a linear penetration depth. This prompted a systematic study of the role of impurities on penetration depth. As a result, detailed studies on single crystals of YBCO with small percentages of zinc or nickel impurities were carried out. It was observed that zinc which introduces strong scattering centers could substantially modify the linear penetration depth into a quadratic behaviour. On the other hand, nickel impurities which act as weak scatterers, were found to hardly change the
linearity of penetration depth. All these results were well explained by a
d-wave scenario of superconducting order parameter.

Further studies of magnetic penetration depth required the oxygen con­
centration of the crystals to be varied in order to probe the superconducting
region of the YBCO phase diagram. This was a simple task for the overdoped
region. However for underdoped crystals, the c-axis contribution to the pene­
tration depth was substantial enough that a method to measure it separately
needed to be developed. As explained in chapter 2, the c-axis penetration
depth as well as the a- and b-axis were extracted from measurements on an
underdoped crystal before and after cleaving it into several smaller pieces
(figs. 2.6 and 2.7). By repeating this procedure for optimal and overdoped
crystals, the entire a-, b-, and c-axis anisotropy of penetration depth was
measured over a wide range of the phase diagram. A wealth of information
was obtained. For example it was found that the temperature dependence of
the c-axis superfluid density bore no resemblance to the linear temperature
dependence for the ab plane at any oxygen concentration. In fact it has a
much weaker temperature dependence at the lowest temperatures, which can
be fit to a power law of about 2.5. These results contradicted earlier measure­
ments of c-axis penetration depth by some other groups as well as theories
based on coherent c-axis transport. It was also observed that by using values
of zero temperature penetration depth (obtained by FIR and \( \mu \)SR) the
c-axis and a-axis superfluid fractions plotted vs \( T/T_c \) have no oxygen doping
dependence and each direction shows a universal behaviour. Later on,
after the c-axis surface resistance was measured by Ahmad Hosseini using a
similar method, the penetration depth results were used to extract the c-axis
conductivity. Given that the nature of c-axis transport in HiTc materials is
still under debate, all these results are of considerable interest to theorists.

During the course of these experiments, an unusual temperature depen­
dence of the penetration depth was observed near the transition temperature.
Further analysis revealed that, unlike low \( T_c \) superconductors which exhibit
mean-field behaviour, the superfluid fraction approaches \( T_c \) not linearly, but
with a slope of 3/2. Careful measurements of penetration depth near \( T_c \) re­
vealed that superfluid response exhibits critical fluctuations consistent with
the 3D-XY universality class. The striking feature was that the critical re­
gion was as large as 10 K. Since reliable results were available to within 0.1
K of \( T_c \), this meant the fluctuations followed 3D-XY behaviour over three
decades in reduced temperature.

During my thesis work, the research in our lab was progressing not only
on the development of new techniques (such as broadband bolometry experiment) but also extensively on crystal growth. The YBCO single crystals grown in yttria stabilized zirconia (YSZ) crucibles by Dr. Ruixing Liang were already of very high purity and homogeneity and recognized world wide as some of the highest quality crystals available. However, there was still room to increase the purity of the crystals by more than an order of magnitude by growing them in BaZrO$_3$ (BZO) crucibles which do not react with the melt during the growth process. After Dr. Liang succeeded in growing single crystals in BZO crucibles, I spent a large amount of time measuring these crystals as a way of characterizing them in order to help the fine tuning of the growth parameters. Eventually, as the best quality single crystals became available, a set of measurements in the optimal and overdoped region were performed. It was observed that the linearity of penetration depth now persisted to our lowest temperature. This confirmed the picture that the previous deviation from linearity was due to impurities in an otherwise pure d-wave superconductor. Our results showed no indication of existence of a second component in the order parameter, as claimed by another group. Also given that the quality of the new crystals was manifestly extremely good, one could conclude that the two order parameter behaviour was unlikely to be intrinsic.

At the time of these measurements, I also managed to improve the sensitivity of our loop-gap resonator to the sample losses by at least an order of magnitude, thereby allowing me to measure, for the first time, the surface resistance of the YBCO crystals at 1 GHz. Simultaneous measurements of penetration depth and surface resistance are extremely desirable as it allows the normal fluid conductivity to be extracted without any approximations. Furthermore combining my penetration depth data with measurements of surface resistance at higher frequencies performed by other students, allowed for the first time a complete spectroscopy of the thermally excited quasiparticles. The temperature dependence of the scattering rate was determined. At low T, the scattering rate levelled off to a value corresponding to an extremely long quasiparticle mean free path. At the same time, the apparent temperature independence was not explainable in terms of point scatterers in a d-wave superconductor. This issue is currently one of the important research interests of the UBC lab.
4.2 Technical Developments

The 1 GHz loop-gap resonator described in chapter 2 along with the sample holder assembly (figs. 2.2 and 2.8), are the main components of the measuring apparatus and their performance directly affects the quality of the results. As explained, a loop oscillator is utilized to monitor the resonance frequency of the resonator as the sample temperature is varied. In the course of the thesis work, the stability of the oscillator was improved by careful lead plating of the resonator in order to obtain higher quality factors (~ $1.5 \times 10^6$). Furthermore, since the resonator is immersed in the liquid helium bath, careful temperature regulation of the bath was instituted to compensate for temperature drifts due to a decrease in the helium level with time or due to heat leak from the sample holder as the temperature of the sample is varied. Finally, the addition of a limiter to the loop oscillator provided better stability in the amplitude of the signal. Overall, these improvements provided stability of the order of 0.1 Hz/minute for the resonator frequency which corresponded to about 0.2 angstrom resolution in penetration depth for a 1mm $\times$ 1mm platelet sample.

Other issues regarding the penetration depth measurements include the background signal, the calibration constant with consideration of thermal expansion effects, and the thermometry. Shortly after the microwave setup was completed, the background signal was obtained by measuring the bare sapphire plate in the same position as in the experiment (fig. 2.9) with a small smear of vacuum grease typical of the amount used for holding the sample in place. It was found that there is a small background signal which increases with temperature and was at the 2% level of the typical measurements on YBCO crystals below 20 K. By replacing the sapphire plate with a higher purity one reduced the background signal to a level below our detection limit. The calibration constant was obtained by measuring lead-tin samples with known DC resistivity. For these samples, after taking the thermal expansion effects into account, it was found that over a wide temperature range above 10 K, $R_s = X_s$ which is expected for a normal metal. The calculated calibration constant was found to be temperature independent, a key requirement if one wants to reliably calculate the penetration depth for samples with various dimensions and aspect ratios.

Thermometry can always be a concern in low temperature measurements. For this work, the most demanding thermometry was for the measurements of critical fluctuation below $T_c$ for YBCO single crystals. Although the critical
region was found to be very wide, almost 10K for optimally doped crystals, it was necessary to obtain data very near $T_c$, at temperature increments of less than 50 mK. Therefore, reliable thermometry was required around 93 K. We achieved this by a careful in situ re-calibration of our Cernox thermometer against liquid oxygen vapor pressure. In addition to thermometry itself, temperature stability could have been a limiting factor. The novel design of the sample holder assembly, consisting of a sapphire block and sapphire plate (fig. 2.8) allowed temperature stability better than 1 mK at low T and about 5 mK near $T_c$.

Another great improvement to our experimental setup was the implementation of time domain techniques enabling us to measure the surface resistance at 1 GHz in the same apparatus. Originally, the loop-gap resonator was designed solely for the precision measurements of magnetic penetration depth. It was assumed that the microwave losses at 1 GHz would be small enough that the resonator would not have enough sensitivity to measure them. The main cause of this limitation is the vibrations (microphonics) which causes the frequency of the cavity to fluctuate and which limits the resolution in the Q of the cavity. To overcome this problem, one either needs a cavity with much higher Q or a way to reduce the effect of microphonics. I managed to make improvements on both issues by increasing the Q of the cavity to above $4 \times 10^6$ after a successful lead plating, and by the use of time domain techniques. In this technique the cavity is pulsed at its resonance frequency for about 50μsec and then the exponential decay of the detected power is observed with time. The relaxation time of the signal is a direct measurement of the Q of the cavity and, because the detected power is only sensitive to the envelope of the decaying signal, is effectively insensitive to the instabilities in resonance frequency of the cavity due to microphonics. We managed to achieve more than a factor of 10 increase in the sensitivity to the microwave losses. As a result, I was able to carry out measurements of surface resistance and penetration depth in the same apparatus, and during the same experimental run which then allows the real part of the conductivity to be extracted reliably. As has been seen in the previous chapter, the existence of these results has been an important contributing factor in the spectroscopy of quasiparticles in YBCO single crystals.

The last note on improvements of the experiment concerns the development of computer code for automated data taking. Initially penetration depth data derived from the loop oscillator was essentially taken manually, using a chart recorder along with manual setting of the temperature on a
resistance bridge and using an analog PID temperature controller. Transmission type data was obtained by a computer to record transmitted power versus frequency using an analog to digital convertor and to save the data for further analysis. However, the measurement still required manual temperature settings, as well as executing the computer program at each step. As a result, an experimental run required continuous attendance for the duration of the experiment which could take many hours. I developed a computer code, using visual basic language, which fully automates the data acquisition. In this program, a sequence of predefined commands is entered into a data file which is then executed one by one by the program. These commands cover all the settings of the experiment such as temperature, microwave power level, type of measurement such as frequency- or time-domain. The program then acquires the data points (for example amplitude vs frequency) and after fitting the points to a predefined function, will save the results in data file. One can also observe live plots of the results in order to assess the state of the experiment. Although this may seem straightforward, it is in fact quite complicated when given the extent of the range of variation in the resonance characteristics as the temperature of the sample is varied. As the sample is heated from the superconducting state to the normal state, the resonance frequency is shifted by more than 100 kHz, and the width of the resonance is increased by about two orders of magnitude, from about 1 kHz to 100 kHz. Therefore the resonance signal can easily move out of the scanning area of the microwave synthesizer as the temperature is varied. A sophisticated algorithm was developed to search for the resonance and once found, adjust it to preset parameters appropriate to the amplitude and width of the resonance. This has allowed the taking of automated measurements over the entire temperature range from 1.2 K to 250K without user intervention. I have developed variations of the program to accommodate other experiments and as a result the program is now widely used in the lab. Finally, a simpler version of the program was developed for automating the loop oscillator measurements.