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MAGNETIC PENETRATION DEPTH STUDIES OF THE
SUPERCONDUCTING ORDER PARAMETER IN Lₐ₂₋ₓSrₓCuO₄ AND
THE SUPERCONDUCTING TO NORMAL STATE TRANSITION IN
YBa₂Cu₃O₇₋₅

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor
of Philosophy in the Graduate School of The Ohio State University

By
Kathleen M. Paget, B. S.

*****

The Ohio State University
1998

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We have explored many aspects of superconductivity in several high Tc cuprates through measurements of the magnetic penetration depth, infrared reflectance, and resistivity. The bulk of this thesis is comprised of two particularly significant sub-projects. This thesis explores the symmetry of the superconducting order parameter in La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) and the extent of the critical region at the superconducting to normal state transition in YBa$_2$Cu$_3$O$_{7.4}$ (YBCO) through measurements of $\lambda(T)$. The temperature dependence and absolute value of $\lambda(T)$ are measured using a two-coil mutual inductance technique. Other investigations including the $\lambda(T)$ of BSCCO, O$_2$ depletion of YBCO, and infrared reflectance of Co doped YBCO are included in the appendices.

The symmetry of the order parameter, $\Delta$, in LSCO is as of yet undetermined. To examine the symmetry of $\Delta$ we have measured $\lambda(T)$ in a series of nine superconducting La$_{2-x}$Sr$_x$CuO$_4$ films with Sr concentrations from $x = 0.135$ to 0.175. $\lambda^2(T) - \lambda^2(0)$ is quadratic in $T$ for $1.3 \, \text{K} < T < 10 \, \text{K}$, which puts an upper limit of about 20 K on a possible isotropic gap. For our films, $\lambda(4 \, \text{K})$ ranges from 4500 to 8400 Å, compared to 2000 Å in bulk samples. The $T_C$'s of the films are less than 31 K while in bulk samples $T_C = 37 \, \text{K}$. The larger magnitude of $\lambda(0)$, reduced $T_C$ and higher resistivity of films relative to bulk...
samples, plus the $T^2$ behavior of $\lambda^2(T) - \lambda^2(0)$, lead naturally to the conclusion that superconductivity in La$_{2-x}$Sr$_x$CuO$_4$ is d-wave.

We have studied the transition region of ten superconducting YBa$_2$Cu$_3$O$_{7.5}$ films through measurement of $\lambda(T)$. Contrary to published results on two YBa$_2$Cu$_3$O$_{7.5}$ crystals, $\lambda(T)$ does not display 3D XY behavior to within 0.5 K of $T_C$ regardless of the sample fabrication technique. Measurements are on films made by sputtering, co-evaporation and pulsed laser deposition. For the samples with the narrowest transitions, as determined from the width of the peak in the real conductivity $\sigma_1(T)$, the superfluid density is linear-in-$T$ to within 0.2 K of $T_C$. Since linearity is expected for meanfield behavior, the critical region in YBCO is less than 0.2K wide.

This work has been supported by the DOE Contract No. DE-FG02-90ER4527 through the Midwest Superconductivity Consortium and AFOSR Grant No. F49620-94-1-0274.
To my husband, Steve,
my children, Julia and Nathan,
my parents, August and Carolyn Pfeifer,
and my parents-in-law Charles and Barbara,
whose love and support have sustained me through to this great accomplishment.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>v</td>
</tr>
<tr>
<td>VITA</td>
<td>vi</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIT OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>CHAPTERS</td>
<td></td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Background</td>
<td></td>
</tr>
<tr>
<td>2.1. High T&lt;sub&gt;c&lt;/sub&gt; Superconductors</td>
<td>3</td>
</tr>
<tr>
<td>2.2. The Magnetic Penetration Depth</td>
<td>7</td>
</tr>
<tr>
<td>3. Experimental</td>
<td></td>
</tr>
<tr>
<td>3.1. Two Coil Mutual Inductance Measurement</td>
<td>13</td>
</tr>
<tr>
<td>3.2. Sample Fabrication</td>
<td>23</td>
</tr>
<tr>
<td>4. LSCO Order Parameter</td>
<td></td>
</tr>
<tr>
<td>4.1. Introduction</td>
<td>33</td>
</tr>
<tr>
<td>4.2. Samples</td>
<td>38</td>
</tr>
<tr>
<td>4.3. Penetration Depth Results</td>
<td>40</td>
</tr>
<tr>
<td>4.4. Conclusions</td>
<td>53</td>
</tr>
<tr>
<td>5. YBCO Superconducting-Normal Transition, Critical Region</td>
<td></td>
</tr>
<tr>
<td>5.1. Introduction</td>
<td>54</td>
</tr>
</tbody>
</table>
5.2. Superfluid Density Near $T_c$ ............................................................... 57
5.3. Conclusions ....................................................................................... 70

APPENDICES

A. Reflectance of Co Doped YBCO .......................................................... 71
B. Oxygen Depletion of YBCO ................................................................. 76
C. Magnetic Penetration Depth in BSCCO ............................................... 84
D. Frequency Dependence of the Conductivity in YBCO ....................... 90

LIST OF REFERENCES ................................................................................. 96
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Tables</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Summary of LSCO Samples reported in this thesis. Sr concentrations are nominal</td>
<td>38</td>
</tr>
<tr>
<td>2. Magnetic Penetration Depths and $T_c$'s of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ from Literature</td>
<td>42</td>
</tr>
<tr>
<td>3. Summary of Pure YBCO Superconducting Films</td>
<td>59</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schematic of experimental setup.</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>Mutual inductance of two coils and YBCO film. The mutual inductance of the two coils and the film drops by a factor of 1000 at the superconducting transition due to the induced supercurrents in the film.</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>Temperature effects of the probe. The probe has a background temperature dependence from the temperature dependence of the conductivity of the copper wires. The slope of the phase from 75 to 300 K is due to the gain of the preamplifier changing as the impedance of the pickup wires change. The decrease in the phase from 60 K to 30 K is due to the change in skin depth of the copper wires in the drive circuit.</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>Radial dependence of induced current density in film. The induced current density, J(r), at the surface of a film with $\lambda = 1500 , \text{Å}$ and coil radius of 1 mm.</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Thickness dependence of induced current density in film. The induced current density as a function of depth in the film, J(z), for a film with $\lambda = 1500 , \text{Å}$ and coil radius of 1 mm calculated at the coil radius.</td>
<td>21</td>
</tr>
<tr>
<td>6</td>
<td>$1/\lambda^2$ vs. T for pure YBCO co-evaporated films. $1/\lambda^2$ is shown for films YA, YB, YC in order of decreasing $1/\lambda^2$ (4 K).</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>$1/\lambda^2$ vs. T for pure YBCO sputtered films. $1/\lambda^2$ is shown for films YD, YE, YF in order of decreasing $1/\lambda^2$ (4 K).</td>
<td>27</td>
</tr>
<tr>
<td>8</td>
<td>$1/\lambda^2$ vs. T for pure YBCO laser ablated films. $1/\lambda^2$ is shown for films YG, YH, YI, YJ in order of decreasing $1/\lambda^2$ (4 K). $1/\lambda^2$ for YH is larger than for YI at 60K.</td>
<td>28</td>
</tr>
</tbody>
</table>
9. Resistivity of pure YBCO. The resistivity is shown for films YD, YF, and YI with linear fits to the data above $T_C$. 

10. $1/A^2$ vs. $T$ for film YC. The temperature dependence of film YC is compared to that of a pure YBCO crystal (filled in circles Hardy et al.).

11. $\lambda(T)$ at low $T$. Film YC is shown with a best fit line from 4 to 20 K $\lambda = 1853 \, \AA + 6.2 \, \AA/K \, T$. A second order polynomial will fit from 4 to 40 K with the best fit $\lambda = 1862 \, \AA + 4.6 \, \AA/K \, T + 0.059 \, \AA/K^2 \, T^2$. Film E is shown with a best fit quadratic of $\lambda = 1722 \, \AA + 0.1219 \, \AA/K \, T + 0.059 \, \AA/K^2 \, T^2$.

12. $1/A^2$ vs. $T$ for $La_{0.85}Sr_{0.15}CuO_4$ taken from the literature. Data are from Shibauchi et al., Kossler et al., Aeppli et al., Jaccard et al., and Li et al. 

13. $\lambda(0)$ for $La_{2-x}Sr_xCuO_4$ as a function of Sr doping, $x$, from the literature. The data from Jaccard et al., were measured in films and have the largest values for $\lambda(0)$ while the rest of the data are from bulk samples.

14. Resistivity vs. $T$ for LB1 ($x = 0.15$), LA ($x = 0.135$), and LC1 ($x = 0.175$).

15. $1/A^2(T)$ vs. $T$ for all nine LSCO films in this study. The labels for the curves are arranged in order of decreasing superfluid density at 1K.

16. $1/A^2(T)$ vs. $T$, normalized so that the data agree at 0.9 $T_C$ and 0.6 $T_C$. The axis on the right has been shifted for clarity and is valid for the upper set of data. The upper data sets are for films LA, LB1, LB4, LB6, and LC1. The lower data sets are for films LB2, LB3, LB5, LC2. The data clearly show two functional forms.

17. Real part of the conductivity, $\sigma_1$, vs. $T$ near $T_C$. $\sigma_1$ is shown for a film with multiple transitions, LC1, and a clean transition, LC2. There is no data shown for LC2 below 25.5 K because the average conductivity is zero but extremely noisy. The dissipation for LC1 extends down to at least 23 K.

18. Quadratic fits to $\lambda^2(T)$ below 10 K. Data are shown for films LB1 ($x = 0.15$), LA ($x = 0.135$), and LC1 ($x = 0.175$). The lower curve shows the % difference between the fit and the data.

19. Exponential fits to $\lambda^2(T)$ below 10K. Data are shown for films LB1 ($x = 0.15$), LA ($x = 0.135$), and LC1($x = 0.175$) with a best fit to the temperature dependence from a BCS isotropic s-wave density of states. The lower curve shows the % difference between the fit and the data.
20. Exponential fits to $\lambda^{-2}(T)$ below 10K. Data are shown for films LB1 ($x = 0.15$), LA ($x = 0.135$), and LC1 ($x = 0.175$) with a best fit to the temperature dependence from an anisotropic s-wave density of states. The lower curve shows the % difference between the fit and the data. .......................... 50

21. $\lambda^{-2}(T)$ for all 10 YBCO films studied. The films, in order of decreasing superfluid density at 4 K are, YD, YA, YB, YE, YC, YG, YH, YI, YJ, YF. Films YA-YC were made by co-evaporation, films YD-YF were made by sputtering, and films YG-YJ were made by laser ablation ........................................... 58

22. $\lambda^{-2}(T)$ for all 10 films normalized in temperature to $T_c$ and in penetration depth to $\lambda^{-2}(0.96T_c)$. All of the films show similar behavior in the range $0.96T_c < T < 0.99T_c$ and appear to be close to linear-in-T. Sample-to-sample variations become evident only within 1 K of $T_c$............................................. 60

23. $P(T) = \frac{1/\lambda^2}{\partial(1/\lambda^2)/\partial T}$ is shown for the three co-evaporated films YC, YB, YA. Linear least squares fits yielding the temperature exponents $2\beta = 1.02, 0.95$ and 0.90 respectively are shown as solid lines. The dashed line represents the linear behavior expected of a 3D $XY$ exponent $2\beta = 0.67$........ 63

24. $P(T) = \frac{1/\lambda^2}{\partial(1/\lambda^2)/\partial T}$ is shown for the three sputtered films YD, YF, and YE. Linear least squares fits yielding the temperature exponents $2\beta = 0.98, 0.80$, and 1.03 respectively are shown as solid lines. The dashed line represents the linear behavior expected of a 3D $XY$ exponent $2\beta = 0.67$........ 64

25. $P(T) = \frac{1/\lambda^2}{\partial(1/\lambda^2)/\partial T}$ is shown for the four laser ablated films YI, YH, YG, and YJ. Linear least squares fits yielding the temperature exponents $2\beta = 0.87, 0.93, 0.78$, and 0.78 respectively are shown as solid lines. The dashed line represents the linear behavior expected of a 3D $XY$ exponent $2\beta = 0.67$................................................................. 65

26. $1/\lambda^2$ vs. $T$ for films LB2 and LC2 near $T_c$........................................................................ 67

27. $P(T)$ for film YB taken in the nonlinear response range. The superfluid density is artificially suppressed, increasing the curvature in $\lambda^3(T)$. A linear least squares fit yields an exponent $2\beta = 0.70$, close to the expected 3D $XY$ result. The inset shows $\lambda^3(T)$ measured both in the linear, 1 mA, and nonlinear, 17 mA, response regimes............................................................... 69
28. Reflectance of YBa$_2$(Cu$_{0.97}$Co$_{0.03}$)$_3$O$_{7-\delta}$ and YBa$_2$(Cu$_{0.97}$Zn$_{0.03}$)$_3$O$_{7-\delta}$ films at 10 K, 100 K, and 300 K. The thick lines are the Co doped sample and the thinner lines are the Zn doped sample. Note that the 300 K reflectance spectra for the Co and Zn doped samples are the same while their 10 K reflectance spectra are very different. The 10 K reflectance for the Co goes to unity, but the 10 K Zn reflectance stays low. The data have been smoothed for clarity.

29. $1/\lambda^2 (T)$ for a YBa$_2$(Cu$_{0.97}$Co$_{0.03}$)$_3$O$_{7-\delta}$ and YBa$_2$(Cu$_{0.97}$Zn$_{0.04}$)$_3$O$_{7-\delta}$ film. Note that $1/\lambda^2$ for the 3% Co film is much higher than $1/\lambda^2$ for the 4% Zn doped film. For comparison, pure films have $1/\lambda^2(4 \text{ K}) = 40 \text{ pm}^2$. The inset shows the mutual inductance as a function of temperature for the Co doped sample.

30. $T_c$ vs.$1/\lambda^2(0)$ For four oxygen depleted films compared to oxygen depleted films of Uemera et al. The filled-in triangles are data for film B which was remeasured a year later with a new probe in its final oxygen state and then reoxygenated.

31. $1/\lambda^2$ vs. $T$ for the oxygen depleted films, A, B, C, of Lee et al.

32. $1/\lambda^2$ vs. $T$ for the 8 oxygen depleted states of film D.

33. $\lambda^2(0)/\lambda^2 (T)$ vs. $T/T_c$ for film D with different O stoichiometry.

34. Thin BSCCO film showing individual layers with different $T_c$ values. The inset is a graph of the phase of $M$. Each peak indicates a transition. The transitions are also visible in the $1/\lambda^2 (T)$ graph. The data were measured at three different drive currents, 300 $\mu$A, 15 $\mu$A, and 5 $\mu$A. The lowest drive current data show the superconducting 2201 layers.

35. $1/\lambda^2(T)$ for BSCCO 2212. In order of decreasing superfluid density the films are B1337, B1248, B1325, and B1336.

36. $\lambda^2(0)/\lambda^2(T)$ vs. $T/T_c$ BSCCO 2212. Data from the same four films of Figure 35 are shown.

37. Low temperature $\lambda$ for BSCCO 2212. The data were fitted from 5 K to 30 K with a best fit quadratic of $\lambda(T)= 2378 \text{ A} +0.13 \text{ A/K}^2 T^2$.

38. Complex conductivity of a pure YBCO film measured at 50 kHz (film1).

39. Complex conductivity of a pure YBCO film measured at 5 kHz and 50 kHz (film2).
40. The real part of the conductivity of a pure YBCO film measured at 1 kHz, 5 kHz, 10 kHz, 50 kHz, and 100 kHz. The peak of the data decrease with increasing frequency (film 2). ................................................................. 94

41. The peak of the real conductivity vs. frequency. $\sigma \sim 1/\omega$ over 4 decades in frequency (film 3). The slope of the straight line is 1 indicating $1/\omega$ behavior. The same result was found in other films. ............................................. 95
CHAPTER 1

INTRODUCTION

There are many interesting unresolved issues in the field of high $T_c$ superconductors. Two issues of particular interest are the symmetry of the order parameter and thermal fluctuation effects. This thesis studies high $T_c$ materials through measurements of the magnetic penetration depth, $\lambda(T)$. In particular, $\lambda(T)$ is used to probe the symmetry of the order parameter in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) and the width of the critical region in $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ (YBCO).

The symmetry of the order parameter is fundamental for understanding the superconducting pairing mechanism. Based on currently available data it seems that the symmetry of the order parameter varies among the cuprates. $^1,^2,^3,^4,^5,^6,^7,^8,^9,^{10}$ Although the symmetry of the order parameter in LSCO is currently unknown, there are several experimental reports that indicate that it is not s-wave in character.$^{11,12,13}$ At low temperatures, the temperature dependence of $\lambda$ has clearly distinguishable limiting functional forms for different order parameter symmetries. While there are published $\lambda(T)$ data for LSCO, it is insufficient for determining the symmetry of the order parameter. In this thesis the symmetry of the order parameter of LSCO is probed through analysis of the
low temperature dependence of $\lambda(T)$ in films. The measurements are made with enough accuracy and precision to draw conclusions about the symmetry of the order parameter.

Thermal fluctuation effects are expected to be enhanced in high $T_C$ materials because they have high $T_C$'s, large $\lambda$'s, and small coherence lengths. It has been proposed that thermal fluctuation effects play an important role at temperatures well away from the transition.\textsuperscript{14,15,16} It is important to establish the width of the critical region since it gives an indication of the overall importance of thermal fluctuation effects. There are two reports of $\lambda(T)$ of YBCO crystals that indicate that the critical region is 5-10 K wide with 3D $XY$ type fluctuations.\textsuperscript{17,18} This width is surprisingly large. If the critical region is this large it would permit the study of critical dynamics. In order to probe critical dynamics or set a limit on the critical region, $\lambda(T)$ is analyzed in the transition region of films made by different fabrication methods.

For this thesis the magnetic penetration depth is measured by using a two-coil mutual inductance technique. This technique was developed in the Lemberger lab by Eric Ulm.\textsuperscript{19} I participated in extending the apparatus to its present state of accuracy which permits the measurement of the absolute value of $\lambda$ as well as the change in $\lambda$ with temperature. Through numerous measurements of films of different sizes and characteristics I established the reproducibility and reliability of the apparatus. The measurement is sensitive enough to observe individual layers in a superconducting film become superconducting as was observed in a thin BSCCO film as described in appendix C. In order to make the measurements that are discussed in this thesis, I made some
modifications to the technique to accommodate the low critical currents of LSCO and the low critical currents in the transition region of YBCO.

We use the BaF$_2$ co-evaporation process for fabricating YBCO films. I optimized the film growth procedure to consistently produce high quality YBCO films. I refined the evaporation rates by making a series of films and adjusting the parameters based on Rutherford back-scattering (RBS) results of those films. RBS results were also used to calibrate the thickness of the films grown. The films that we currently produce have a $T_C$ above 90 K and a magnetic penetration depth less than 2000 Å.

For the LSCO study I measured $\lambda(T)$ for nine LSCO films that were provided by the group of Peter Lindenfeld at Rutgers University. For the transition study I measured $\lambda(T)$ of ten YBCO films, three of which I fabricated by co-evaporation. The sputtered films were provided by Brent Boyce, also in the Lemberger group, and the laser ablated films were from two sources, NIST and Wright Patterson Air Force Base. In addition, I measured the resistivity of two of the YBCO films.

Although the bulk of this thesis presents only two studies of $\lambda(T)$, there were several other studies of high $T_C$ materials with which I was involved. I measured $\lambda(T)$ of oxygen depleted YBCO, BSCCO, and BSCCO magnetic multilayers. I measured the complex conductivity as a function of frequency in BSCCO and YBCO at the superconducting to normal transition as well as the infrared reflectance of Co doped YBCO. Some of these projects are discussed in the appendices. The two projects discussed in the text of the thesis are of particular significance and therefore receive the majority of the attention.
CHAPTER 2

BACKGROUND

2.1 High Tc Superconductors

High temperature superconductivity was discovered in \( \text{La}_{2-x}\text{Ba}_x\text{CuO}_4 \) in 1986 and was followed by the rapid discovery of many similar compounds within the same cuprate family.\(^{20,21}\) These compounds are novel because of their high \( T_c \), large anisotropy, and small coherence lengths.\(^{22}\) Due to these properties, cuprates exhibit many differences from conventional superconductors. In at least some of the cuprates, the superconducting pairing in these materials is fundamentally different from low \( T_c \) materials.\(^1,5\) A complete understanding of these materials is still under investigation.

The cuprates are so named because of the Cu-O planes which exist in each compound. Some of the most studied cuprates are \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) (YBCO), \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) (LSCO), \( \text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8 \) (BSCCO), and \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 \) (NCCO). The cuprates are layered compounds with the Cu-O planes stacked along the c-axis. This layering creates a large c axis lattice constant which leads to a large anisotropy in electronic properties. The Cu-O planes are responsible for the bulk of the superconductivity in these compounds. The superconducting carriers are mobile holes in the planes except in NCCO which has
electron carriers. In addition to the Cu-O planes, YBCO has superconducting Cu-O chains which act as a reservoir for charge. The chain layers cause YBCO to have an orthorhombic crystal structure with very similar a and b lattice parameters, a = 3.81 Å and b = 3.88 Å which causes twinning. The other cuprates have tetragonal crystal structures.

The optimal transition temperatures of the cuprates are 38 K, 92 K, 97 K, 24 K for LSCO, YBCO, BSCCO, and NCCO respectively. The transition temperature can be varied by doping and shifting the oxygen concentration. Doping shifts $T_C$ either through the effects of disorder or through a direct change in the carrier concentration. Oxygenation directly changes the hole concentration in YBCO as does Sr doping in LSCO. It is possible to shift the compounds away from optimal doping which is defined as the doping level with the maximum $T_C$ and access the underdoped and overdoped portions of the phase diagram.

Conventional superconductors are well described by the BCS theory of electron-phonon mediated singlet pairing. Since the theoretical transition temperature is limited by the phonon frequencies that participate in pairing, the high transition temperatures of the cuprates suggest that another type of coupling is responsible for their superconducting properties. One proposed pairing mechanism for the cuprates is antiferromagnetic spin fluctuations.

The superconductors with electron phonon coupling have an s-wave order parameter, $\Delta(k)$. It is possible for electron phonon coupling to produce either an isotropic s-wave or an anisotropic s-wave order parameter. An isotropic order parameter is independent of $k$, where $k$ is a wave vector in momentum space, while an anisotropic s-
wave order parameter has a magnitude that varies as a function of $k$, but a constant phase. Antiferromagnetic spin fluctuations are predicted to produce an order parameter with d-wave symmetry. The $k$ dependence for a generic $d_{x^2-y^2}$ order parameter is given by $A_k = \Delta_0[\cos^2(k_x) - \cos^2(k_y)]$. This order parameter has line nodes, where $\Delta_k$ is zero and the phase of $\Delta$ changes by 180 degrees across the nodal lines. Determination of the symmetry of the order parameter gives insight into the possible pairing mechanisms for superconductivity.

It is generally accepted that YBCO has a predominately d-wave order parameter. There are two types of measurements that are used to determine the order parameter symmetry. The first are experiments that look for nodes in $\Delta$ through superconducting properties that depend on the density of states. The second type of experiment directly probes the phase of $\Delta$. Measurements of the magnetic penetration depth, angle resolved photo emission, NMR relaxation rate, and infrared reflectance of YBCO are consistent with a gapless or nearly gapless density of states. Either a d-wave or an anisotropic s-wave order parameter could exhibit a nearly gapless density of states. Phase sensitive measurements such as corner squids, and tri-crystal flux rings, show that the phase of the order parameter changes sign as a function of $k$ eliminating an anisotropic s-wave order parameter for YBCO.

Another difference of the cuprates from conventional superconductors is their short coherence lengths. One consequence of their short coherence lengths is that the cuprates are Type II superconductors and therefore have a vortex lattice phase. Another result of short coherence lengths is that the order parameter is less rigid which leads to enhanced thermal fluctuations. Fluctuations dominate in a critical region near $T_c$,.
although in low \( T_c \) materials the critical region is much too narrow to probe. Enhanced fluctuations in the cuprates may permit an observation of critical dynamics.

In the critical region the behavior of the superconducting properties will be dictated by the universality class of the system. The universality class is determined by the dimensionality of the order parameter and the dimensionality of the fluctuations according to renormalization group theory.\(^\text{32}\) The dimensionality of the order parameter is assumed to be 2 since it is a complex scalar. The dimensionality of the fluctuations is less clear. In films, thin compared to the coherence length, the fluctuations are clearly 2D. In bulk samples which could have 3D fluctuations, the fluctuations may be 2D due to the weak c-axis coupling. If layers become decoupled near \( T_c \) the superconductor may crossover from 2D to 3D fluctuations. The effective thickness of a decoupled sample would be the c-axis lattice constant.

Discovery of these novel compounds has opened the door for the exploration of new physics. Two areas of study include the symmetry of the superconducting order parameter and thermal fluctuation effects. This thesis will use the magnetic penetration, \( \lambda \), depth to probe the symmetry of the order parameter of LSCO and fluctuation effects at the superconducting-normal transition in YBCO.
2.2 The Magnetic Penetration Depth

The magnetic penetration depth, $\lambda$, is a fundamental parameter in superconductivity. It is defined as the distance over which the magnetic field decays in a superconductor. In the London approximation $1/\lambda^2 \sim n_e$ where $n_e$ is the total electron density. In practice, the total electron density is only an upper bound, and $1/\lambda^2(0)$ can be modified by scattering or magnetic impurities.

The interpretation of the temperature dependence of $1/\lambda^2$ contains a wealth of information both at low $T$ and near the transition. The penetration depth has proven to be critically important in understanding the superconducting state, because unlike other experimental quantities, there is no normal-state background associated with $\lambda(T)$. At low temperatures the dominant temperature dependence is determined by the density of states, although this can be modified in the event of very strong thermal fluctuations. For temperatures very close to $T_c$ critical fluctuations dominate the temperature dependence of $\lambda$.

In the clean limit of BCS theory the temperature dependence of the penetration depth can be calculated from

$$\frac{\lambda^2(0)}{\lambda^2(T)} = 1 - 2\int_0^\infty \left(-\frac{\partial f}{\partial E}\right) \frac{N_s(E)}{N(0)} \, dE$$

(1)
where $N(E)$ is the density of states and $f$ is the Fermi function. An isotropic s-wave order parameter has a fully formed gap in the density of states which leads to an exponentially activated behavior as $T/T_C$ goes to 0 K,

$$\frac{\lambda^2(0)}{\lambda^2(T)} = 1 - \frac{2\pi \Delta}{k_B T} e^{\frac{-\Delta}{k_B T}}$$ \hspace{5cm} (2)$$

For a BCS isotropic weak coupling order parameter $\lambda^2$ will be essentially flat until $T \geq 20\% T_C$ and then it will begin to decrease rapidly with $T$. An anisotropic s-wave superconductor will still have an exponential temperature dependence consistent with the minimum value of $\Delta_k$ although the term preceding the exponential will depend on the specific shape of $N(E)$.

The $d_{x^2-y^2}$ order parameter has a linear density of states at low energies which leads to a linear $T$ dependence in $\lambda$ at low temperatures. Since $\lambda$ depends only on the order parameter through $N(E)$, the phase of the order parameter is not directly probed, only the integrated magnitude. Further insight into the underlying symmetry of the order parameter can be obtained from the penetration depth through the effects of disorder on the density of states as is more fully explained in Chapter 4.

In the transition region the Ginzburg-Landau theory can be applied. The free energy is expanded in terms of the order parameter, $|\psi|^2$, which is proportional to $n_e$. In the absence of fields or gradients the free energy density is given by
The minimum of the free energy determines the equilibrium value of the order parameter,

\[ f_s - f_n = a|\psi|^2 + \frac{\beta}{2}|\psi|^4 + O(|\psi|^6) \]  

(3)

The magnitude of the thermal fluctuations can be determined from equating the energy of the fluctuation to the available thermal energy of the system, \( k_B T \). The Ginzburg criterion is defined as the temperature where the size of the fluctuation of the order parameter becomes comparable to the magnitude of the order parameter. This criterion gives an approximation for where the Ginzburg Landau theory is no longer complete and critical fluctuations must be considered. The predicted width of the critical region from the Ginzburg criterion (in MKS units) is

\[ \Delta T \leq \frac{2\pi^2 \mu^2 (k T_{c0})^2}{\Phi_0^2} \left( \frac{\lambda(0)^2}{\xi(0)} \right)^2 T_{c0}, \]  

(5)
where $\Phi_0$ is the superconducting flux quantum, $\xi(0)$ is the Ginzburg Landau coherence length at zero temperature, and $T_{co}$ is the MF transition temperature. We note the strong dependence of the width of the critical region on the zero temperature penetration depth $\lambda(0)$; therefore, we expect a dramatic increase in fluctuation effects as $\lambda(0)$ is increased. Assuming optimistic values of $\lambda(0) = 2000 \text{ Å} \text{ and } \xi = 10 \AA \text{ for YBCO}$, the Ginzburg criterion predicts a critical region width $\Delta T \sim 0.4 \text{ K}$. For more conventional values of $\lambda(0) = 1400 \text{ Å} \text{ and } \xi = 14 \AA \text{, } \Delta T \sim 0.05 \text{ K}$. Since the Ginzburg criterion is constructed in such a way as to indicate an approximate critical region width, this low estimation does not preclude a 5 K wide critical region. Measurements of fluctuation effects in conventional superconductors are experimentally inaccessible making further phenomenological refinements of the Ginzburg criterion difficult.

In the critical region a 2D sample should exhibit a Kosterlitz-Thouless (KT) transition which is a vortex unbinding transition. If the layers in a high $T_c$ superconductor are decoupled, then the even a thick sample could exhibit a KT transition. A KT transition is characterized by an abrupt drop to zero in the superfluid density at a temperature given by

$$\frac{2\lambda^2 T_{KT}}{d} = 19.6 \text{ mmK} \quad (6)$$

where $d$ is the thickness of the film. In a high $T_c$ superconductor with decoupled layers, $d$ would be equal to the $c$ axis lattice parameter.
For the 3D $XY$ universality class the superfluid density is suppressed from the mean field value but not as dramatically as in the KT transition. The predicted temperature dependence of a 3D $XY$ transition is: $\lambda^{-2} \sim (T_C - T)^{0.67}$. There are other possible temperature dependences for $\lambda(T)$ when one considers granularity or a spread in properties through the thickness of the film. These different temperature dependences cannot hide a 3D $XY$ transition and make $n_e$ appear linear in $T$. 
3.1 Two Coil Mutual Inductance Measurement

The complex conductivity of thin superconducting films can be determined from their response to an applied AC field. We measure the complex mutual inductance of two coils with the film centered coaxially between them. When the geometry is well defined it is possible to calculate the complex conductivity of the film.

The probe and coil forms are made from nylon. The probe end is made from a single nylon block where the location for the coils and the screw holes are drilled before the block is cut in half. This ensures coaxial alignment of the coils. A centering ring is milled into the block to assist in accurately centering the film in the probe. The receive coil is fully embedded in the nylon block and the drive coil adjusts so that it can be held tightly against the film to minimize the gap between the coils.

In order to accurately extract the complex conductivity from the mutual inductance, the fields from the coils should be minimized for radii greater than the film radius. Two of the drive coil geometries that accomplish this are a quadrupole coil or a dipole pancake coil. The coils used in this experiment are 4 layer quadrupoles with 80
turns that are wound from 0.0762 mm diameter copper wire. The coils are wound under a microscope to ensure that the windings are all parallel to each other. The coils have a 1.05 mm radius and are 1.5 mm long. With a 1 mm gap the mutual inductance of the two coils is 60 nH.

It is important to minimize all sources of stray coupling and cross-talk between the drive and receive coils. The leads from the coils are twisted together to minimize stray coupling. The twisted leads from the drive and the receive coils are brought along opposite sides of the nylon block to where they are soldered to the probe wires. The loop at that solder joint is also minimized. The probe leads are varnished twisted pairs which are housed in two guide tubes along the length of the probe that keep the twisted pairs separated. The wires exit the probe at BNC connectors that are housed in two separate brass blocks.

A schematic drawing of the setup is shown in Figure 1. An AC signal generator is used to produce a drive current that ranges from 1-100 kHz. A 1 kΩ resistor in series with the probe is used to maintain a stable current as the temperature of the probe is varied. Typical operating drive currents are between 100 μA and 10 mA, although as low as 5 μA can be used. The current in the drive circuit is measured from the voltage across a mutual inductor of known inductance of 20 μH. The inductive voltage is measured with a single phase lock-in amplifier since the phase of the signal is constant during the measurement.
Figure 1. Schematic of Experimental Setup.
The pickup circuit consists of an Ithaco 565 Low Noise Preamplifier, an EG&G PAR model 113 preamplifier with a band bass filter, and a SR830 DSP Lock-in Amplifier. The Ithaco 565 has a transformer input mode which greatly reduces the noise and it was important in detecting the signal when the measurement was made with low currents as was necessary in the transition region and for LSCO. It is crucial to be able to change the sensitivity ranges on the lock-in amplifier during the measurement. The pickup voltage typically drops by factor of 1000 at the superconducting transition and, by changing the sensitivity ranges, the voltage can be accurately measured (see Figure 2). The data are collected using GPIB communication with programs written in visual basic by Aaron Pesetski and Brent Boyce.

The experiment is performed in a standard LHe dewar. The outer LN$_2$ jacket is left empty, and LHe is blown at the probe until the desired temperature is reached. The probe warms slowly enough so that the data can be recorded continuously. Temperatures lower than 4 K can be reached using a stokes pump on a LHe bath. The dewar is filled with LHe and the LN$_2$ jacket is still left empty. The Stokes pump reduces the pressure to about 10 Torr which corresponds to an equilibrium temperature of 1 K. When the Stokes pump is closed the temperature rises and once again data can be collected.

There are two temperature-dependent background effects associated with the probe which are caused by the temperature dependence of the conductivity of the copper wires. The first effect is caused when the skin depth in the copper wires becomes comparable to the diameter in the wires. The position of the drive currents changes from being located at the outer edge of the wires to being distributed thorough out the wires.
Figure 2. Mutual inductance of two coils and YBCO film. The mutual inductance of the two coils and the film drops by a factor of 1000 at the superconducting transition due to the induced supercurrents in the film.
Figure 3. Temperature Effects of the Probe. The probe has a background temperature dependence from the temperature dependence of the conductivity of the copper wires. The slope of the phase from 75 to 300 K is due to the gain of the preamplifier changing as the impedance of the pickup wires change. The decrease in the phase from 60 K to 30 K is due to the change in skin depth of the copper wires in the drive circuit.
This effect is noticeable around 60 K and cause a change in magnitude of 0.1% and a change in phase of 1°; see Figure 3. The second effect is due to the change in impedance of the pickup coil and leads. The 565 preamplifier has a low input impedance in the transformer mode, and for frequencies larger than 40 kHz the magnitude and phase of the gain are very sensitive to the input impedance. The effect is most noticeable in the phase of the measured mutual inductance which decreases linearly by three degrees with temperature from 100 - 300 K. At low temperatures, T < 25K, both of these effects are negligible. Frequencies around 20 kHz and lower minimize both of these background effects. Wire diameters can also be altered to minimize this effect. To correct for the background, the temperature dependence of the mutual inductance of the probe with a blank substrate is measured, and the film data is corrected using this background file.

The complex conductivity must be extracted from the corrected mutual inductance data. Maxwell's and London's equations are solved self-consistently to find the field due to the film with a given complex conductivity and the drive current. The calculation assumes an infinite area film. The induced current density is shown in Figure 4 for a film with d = 1000 Å, and λ = 1500 Å. The peak in the current density is at a distance r slightly larger than the coil radius. Early calculations were made by assuming that the current density was independent of thickness over an effective thickness in the film as a function of λ. The calculation has recently been improved to include the variation of the current through the thickness of the film. The effect of neglecting the correct thickness calculation can be determined from comparing \( M = \alpha \lambda / \tanh(d/\lambda) \) to \( M = \text{sech}(d/\lambda) \alpha \lambda / \tanh(d/\lambda) \) where the \( \text{sech}(d/\lambda) \) is the approximate
Figure 4. Radial dependence of induced current density in a thin film. The induced current density, $J(r)$, at the surface of a film with $\lambda = 1500 \, \text{Å}$. The coil is counter-wound (quadrupole) with 80 turns and a radius of 1mm.
Figure 5. Thickness Dependence of Induced Current Density in a Thin Film. The Induced current density as a function of depth in the film, $J(z)$, for a film with $\lambda = 1500\text{Å}$. The coil is counter-wound (quadrupole) with 80 turns and a radius of 1mm.
result of the thickness correction. \( M \) is the mutual inductance, \( d \) is the film thickness, and \( \alpha \) is a constant that depends on the coil geometry. The hyperbolic secant term becomes important when \( \lambda \) is on the order of or smaller than \( d \). Figure 5 shows the variation of the induced current density as a function of distance, \( z \), through the thickness of the film.

A table of \( M(\sigma_1, \sigma_2) \) is calculated for the entire range of \( \sigma_1 \) and \( \sigma_2 \) that are detectable with the coils. A look-up routine is used to invert the measured \( M(T) \) data to determine \( \sigma_1(T) \) and \( \sigma_2(T) \) from measured \( M(T) \) data. All of the imaginary conductivity is assumed to be due to the magnetic penetration depth, so \( 1/\lambda^2 \) is given by \( \sigma_2/\mu_0 \omega \). This is clearly valid when \( \sigma_1 = 0 \), but care must be taken in interpreting \( 1/\lambda^2 \) when \( \sigma_1 > 0 \).

In order to correct for the finite area of the film a calibration constant, called the zero position, is determined for each film shape. The calibration constant is then subtracted from the mutual inductance measured from the film. The mathematics and the accuracy of the subtraction procedure have been calculated by Turneaure et al.\textsuperscript{40,41}

To determine the zero position the mutual inductance of the probe with thick Pb foil of the same shape as the film is measured at 4K. Since the Pb foil is much thicker than the penetration depth this is equivalent to measuring the signal with \( \lambda = 0 \), which should be zero for an infinite film. This zero position is a measure of the voltage due to the field that "goes around" a finite film and it is subtracted from the mutual inductance measured for a sample. This allows us to determine the absolute value of the penetration depth in addition to the temperature dependence.

3.2 Sample Fabrication
High Tc superconductors are easily made in large quantities of pressed powder, but these samples are composed of large randomly oriented grains that are not well connected. Single crystals are difficult to grow and they are typically very small (0.5 mm x 0.5 mm x 1 μm). Thin films are advantageous for studying the properties of high Tc materials because they can be grown well oriented with very large surface areas. Films are also interesting from a technological standpoint since there are applications for thin films in the microelectronics industry.

The three main growth techniques for high Tc thin films are co-evaporation, sputtering, and laser ablation. Films fabricated by different growth techniques have different microstructures and slightly different properties. This can be useful for comparing results for disorder-dependent effects.

The co-evaporated films were made at OSU by the BaF₂ process. Cu, Y, and BaF₂ are simultaneously evaporated in a vacuum while O₂ is bled into the chamber. The deposition rates of each source are controlled by a feedback loop employing Inficon crystal sensors to determine the rates. The recipe for co-evaporated films has been refined using RBS results to fine tune the stoichiometric rates.

The best quality films are grown on SrTiO₃ substrates that are polished with a final chemical etch stage at Marketec Inc. The surfaces are reported to be smooth to 2.4 Å. The substrates are cleaned prior to deposition. The substrates are vibrated in a beaker of trychloroethylene (TCE) in a sonic cleaner for 4 min. The TCE cleaning is followed by identical cleanings with acetone and then isopropyl alcohol. For the final stage the
substrates are held in a beaker of water in the sonic cleaner. The substrates are baked for 30 min. at 150°C.

The deposition chamber has four sources. The three resistively heated boats are used for Cu, BaF₂, and a possible dopant. The fourth source, Y, is evaporated by an electron gun. BaF₂ is sublimated from a SiO style boat which has baffles for maintaining a stable deposition rate. Equally important for stable BaF₂ evaporation is the loading of the boat. Optimal stability is obtained when small pieces (2 - 5 mm in diameter) but not dust of BaF₂ are used to fill the side chambers of the boat ¾ full. Y and Cu are very amenable to evaporation and their rates are easily stabilized. The Y crucible is weighed and refilled if necessary before each deposition to maintain the same level of Y so the measured rate at the crystal sensor will be correctly calibrated. The deposition rates are 7.7 Å/s, 2.3 Å/s, 2.5 Å/s for BaF₂, Cu and Y respectively. The total thickness of the film calculated from the rates agrees well with the thickness as determined by RBS. The thickness of a film is equal to 1.5 times the thickness on the BaF₂ sensor.

The 15 mm diameter substrates are mounted face side down in a rotator which revolves at 0.5 rev/sec which corresponds to about two unit cells deposited per revolution. The O₂ is bled into the chamber using a needle valve and through a nozzle which is located 4 cm from the substrates without casting a shadow on the substrates. During deposition the pressure is maintained at 3.2 x10⁻⁶ Torr by throttling the ion pump while the O₂ is bled in. The base pressure in the vacuum chamber before deposition is typically 7 x 10⁻⁷ Torr.

After deposition the chamber is allowed to cool for 10 min. before the substrates are removed and annealed in a programmable tube furnace. The anneal sequence is 880°
C in flowing wet $O_2$ for 90 min followed by a $450^\circ C$ dwell in dry $O_2$. The high
temperature wet anneal removes the fluorine and permits epitaxial growth. The $450^\circ C$
dwell is the final oxygenation step. Co-evaporated films typically have chimney defects
which are observed by atomic force microscopy (AFM). The chimneys are believed to be
formed by the fluorine as it leaves the films.

This procedure reliably produces films with $T_c$'s greater than 90 K and high
superfluid densities for film thicknesses around 1000-1500 Å; see Figure 6. Thick films ($d$
> 2500 Å) become difficult to grow because as the sources begin to run out the rates
fluctuate. Another advantage of co-evaporated films is that it is easy to incorporate
dopants into the films although it becomes difficult to control the rates for small dopant
levels.

Sputtered films typically exhibit $T_c$'s a few degrees lower than co-evaporated
films; see Figure 7, but they have cleaner surfaces. Laser ablated films have similar $T_c$'s to
co-evaporated films; see Figure 8. They both have the advantage of being annealed in
situ. Two disadvantages of sputtering are that deposition rates are much smaller, typically
100Å/hr and a new target must be made for each new composition desired. For a
complete discussion of the sputtering parameters see Boyce et al. Laser ablated films also
require a new target for each desired composition. 42,43

From the resistivities measured on a few of our YBCO samples we can see that
they have the characteristic linear temperature dependence and sharp resistive transitions;
Figure 6. $1/\lambda^2$ vs. T for pure YBCO co-evaporated films. $1/\lambda^2$ is shown for films YA, YB, YC in order of decreasing $1/\lambda^2$ (4 K).
Figure 7. $1/\lambda^2$ vs. T for pure YBCO sputtered films. $1/\lambda^2$ is shown for films YD, YE, YF in order of decreasing $1/\lambda^2$ (4 K).
Figure 8. $\frac{1}{\lambda^2}$ vs. $T$ for pure YBCO laser ablated films. $\frac{1}{\lambda^2}$ is shown for films YG, YH, YI, YJ in order of decreasing $\frac{1}{\lambda^2}$ (4 K). $\frac{1}{\lambda^2}$ for YH is larger than for YI at 60K.
see Figure 9. There is no residual resistivity as determined from the linear extrapolation to $T = 0$ K which indicates that the disorder in the films is minimal.

Another measure of the quality of the films is the temperature dependence of the penetration depth. Since YBCO is a d-wave superconductor, for low $T$ it should have a linear temperature dependence of $\lambda$ for clean samples and a quadratic dependence for dirty, or disordered samples. At low temperatures the co-evaporated films frequently have linear $\lambda$'s as can be seen in Figure 6. The overall temperature dependence of $\lambda^{-2}$ in the co-evaporated films is very similar to that measured in crystals; see Figure 10. The slope of the linear term is 6 Å/K which is typical of the slope seen in data from crystals, see Figure 11. Although both laser ablated and sputtered films can have low penetration depths at $T = 4$ K, which is a sign of minimal disorder, they all have quadratic temperature dependences for their low temperature $\lambda$'s. If this is due to disorder in a d-wave superconductor then the films with the quadratic $\lambda(T)$ should all have larger $\lambda(0)$ then the linear $\lambda(T)$ films. Since co-evaporated films have a different microstructure from sputtered or laser ablated films it seems likely that some types of disorder have a stronger effect than others on filling in the density of states.
Figure 9. Resistivity of pure YBCO. The resistivity is shown for films YD, YF, and YI with linear fits to the data above $T_c$. 
Figure 10. $1/\lambda^2$ vs. $T$ for film YC. The temperature dependence of film YC is compared to that of a pure YBCO crystal (filled in circles Hardy et al.$^3$)
Figure 11. $\lambda(T)$ at low $T$. Film YC is shown with a best fit line from 4 to 20 K, $\lambda = 1853 \, \text{Å} + 6.2 \, \text{Å}/K$. A second order polynomial will fit from 4 to 40K with the best fit $\lambda = 1862 \, \text{Å} + 4.6 \, \text{Å}/K + 0.059 \, \text{Å}/K^2 \, T^2$. Film YE is shown with a best fit quadratic of $\lambda = 1722 \, \text{Å} + 0.1219 \, \text{Å}/K^2 \, T^2$. 

32
CHAPTER 4

LSCO ORDER PARAMETER

4.1 Introduction

A fundamental question in the high-T_c cuprate superconductors is the symmetry of the order parameter. The order parameter may differ among the cuprates despite the commonality of quasi-two-dimensional copper-oxide planes. There is a strong consensus that YBa_2Cu_3O_7 (YBCO) and Bi_2Sr_2CaCu_2O_x (BSCCO) have d-wave order parameters, but there is evidence that Nd_{2-2x}Ce_xCuO_4 (NCCO) has an s-wave order parameter. The question remains whether La_{2-x}Sr_xCuO_4 (LSCO) manifests d- or s-wave symmetry. LSCO's crystal structure and T_c are similar to NCCO. However, LSCO is hole doped like YBCO and BSCCO while NCCO is electron doped. Previous studies of Raman spectra, infrared reflectance, neutron scattering, and heat capacity of LSCO have found results that are inconsistent with a simple isotropic s-wave gap. We have studied the symmetry of the gap using the magnetic penetration depth, \lambda(T).

The magnetic penetration depth reflects the symmetry of the order parameter primarily through its dependence on T at T/T_c << 1. The distinction between d-wave and s-wave symmetries is well defined and experimentally accessible, particularly when there is
some disorder in the sample. For an anisotropic superconductor with a nonzero minimum energy gap, $\Delta_{\text{min}}$, in its excitation spectrum, $\lambda(T)$ is clearly exponential, $\lambda^{-2}(T) - \lambda^{-2}(0) \sim e^{-\Delta_{\text{min}}/kT}$, for $kT$ less than about $0.1\Delta_{\text{min}}$. For an isotropic BCS superconductor with a square-root singularity in its density of states at $E = \Delta$, exponential behavior persists up to about $0.3\Delta$. The exponential behavior is not affected by nonmagnetic disorder or by small levels of magnetic disorder, although the magnitude of $\Delta$ generally is affected. In fact, if the s-wave gap is anisotropic, then disorder tends to make it isotropic, thereby increasing $\Delta_{\text{min}}$ and making the exponential behavior in $\lambda(T)$ more prominent. Small levels of magnetic disorder smear out the singularity in the density of states and reduce $\Delta$.

For a d-wave order parameter, $\lambda^{-2}(T)$ is linear in $T$, i.e., $\lambda^{-2}(T) - \lambda^{-2}(0) \sim T$, for very clean samples, and it is quadratic, $\lambda^{-2}(T) - \lambda^{-2}(0) \sim T^2$, for disordered samples. Only a very few pure YBCO and BSCCO single crystals exhibit a linear low $T$ penetration depth, presumably due to the sensitivity of the density of states to small amounts of disorder. Most crystals show quadratic behavior, even nominally excellent crystals with very sharp transitions and low resistivities. None show gap-like behavior. By contrast, in three NCCO films, $\lambda$ is reported to be exponentially activated.

$\lambda$ also should reflect the symmetry of the order parameter through the effects of disorder on its magnitude. $\lambda(0)$ in d-wave superconductors is predicted to increase rapidly with disorder. In an s-wave superconductor it is insensitive to disorder until the electron mean free path is suppressed below the Ginzburg-Landau coherence length, $\xi_0$. In
cuprates $\xi_0$ is so short, about 15Å, that the electron mean free path is generally larger than $\xi_0$, and, therefore, the effect is small.

Since we draw conclusions from data on LSCO films, it is germane to note how studies of YBCO films compare with YBCO crystals. Some films made by co-deposition of Y, BaF$_2$, and Cu with a high temperature post-anneal in flowing oxygen show linear behavior of $\lambda$ with $T$ from 30K down to at least 2K, with a slope and magnitude close to crystals as was discussed in Chapter 3. This indicates that it is possible to make films of similar quality to crystals, despite the many grain boundaries, strain due to lattice mismatch with the substrate, and disorder incorporated during deposition. Many films made by co-deposition, and essentially all films made by sputtering and by pulsed laser deposition, show $T$-squared behavior below about 30 K, presumably due to a small amount of disorder incorporated during deposition. There is one report of gap-like behavior in films. YBCO films doped with 3%-6% Ni and Zn are substantially disordered, and they have greatly reduced superfluid densities, quadratic $T$-dependencies, and reduced transition temperatures, as expected for a d-wave order parameter.

There are several published magnetic penetration depth studies of LSCO. $\lambda(T)$ of La$_{0.85}$Sr$_{0.15}$CuO$_4$ from $\mu$sr, microwave surface impedance, magnetization measurements, and two-coil mutual inductance measurements is presented in Figure 12. The best low-$T$ data seem to be from the $\mu$sr measurement on bulk material by Aeppli et al., which are smooth and monotonic at low $T$. Their data show that $\lambda(T)$ is not linear over the range for which YBCO crystals are linear, namely, below $T_C/3$. 35
Figure 12 $1/\lambda^2$ vs. $T$ for La$_{0.85}$Sr$_{0.15}$CuO$_4$ taken from the literature. Data are from Shibauchi et al.,$^{56}$ Kossler et al.,$^{53}$ Aeppli et al.,$^{52}$ Jaccard et al.,$^{58}$ and Li et al.$^{57}$
However, with only three data points at low T, it is not possible to differentiate between quadratic and exponential dependence. In contrast the data presented here extend to 1.3 K and have a noise level of 1 Å in λ, thereby making it possible to distinguish among an exponential, quadratic, or a linear T dependence at low T. Only after years of painstaking efforts towards maximizing sample quality was it possible to observe a linear T dependence in λ(T) for YBCO. Unless further efforts also make this possible in LSCO, the debate between d-wave and s-wave symmetry in LSCO may have to be decided by distinguishing between quadratic and exponential behavior in λ.

The superconducting properties of LSCO films are generally different from bulk samples. A summary of reported values of λ(0) and Tc for the optimally doped compound, La1.85Sr0.15CuO4, is shown in Table 1. Optimally doped sintered pellets and crystals have Tc’s around 37 K and λ(0) ≈ 2500 Å. Films typically have lower Tc’s and larger penetration depths. Our films have Tc’s from 23 K to 30 K and λ(0) from 5000 Å to 8000 Å. Jaccard et al. reported films with Tc = 20.9K and λ(0) ~ 7000 Å. The differences between films and bulk materials are attributed to disorder, strain, and oxygen vacancies in the films. Since disorder is expected to enhance gap-like behavior in anisotropic s-wave superconductors, disorder in films plays a positive role in the present task of distinguishing d-wave from s-wave order parameters.

A discussion of the dependence of λ(0) on Sr concentration fills in the background on the current state of knowledge about λ in LSCO. By varying the Sr concentration both the underdoped and overdoped regimes are readily accessible in LSCO. Sr doping increases the normal state carrier density. Tc increases with increasing Sr until optimal
doping at $x = 0.15$. It is well established that in the underdoped region, $x < 0.15$, the superfluid density, $n_s \sim \lambda^2$, increases as $x$ increases toward 0.15 (Figure 13). For Sr concentrations above $x = 0.15$, literature results are inconclusive. The most extensive study on the effect of Sr doping on the superfluid density was done by Locquet et al., who found a maximum in the superfluid density at optimal doping in thin films. Measurements on overdoped sintered pellets find that the superfluid density is relatively unchanged from optimally doped samples.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Experiment</th>
<th>Sample</th>
<th>$T_C$ (K) $x = 0.15$</th>
<th>$\lambda(0)$ (Å)</th>
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<tr>
<td>Uemera et al.</td>
<td>µsr</td>
<td>sintered pellets</td>
<td>37</td>
<td>2040</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>2700</td>
</tr>
<tr>
<td>Kossler et al.</td>
<td>µsr</td>
<td>sintered pellets</td>
<td>37</td>
<td>2000</td>
</tr>
<tr>
<td>Aeppli et al.</td>
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<td>sintered pellets</td>
<td>37</td>
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<tr>
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<td>sintered pellets</td>
<td>38</td>
<td>2200</td>
</tr>
<tr>
<td>Locquet et al.</td>
<td>two coil method</td>
<td>films</td>
<td>22</td>
<td>7000</td>
</tr>
<tr>
<td>Shibauchi et al.</td>
<td>microwave surface</td>
<td>single crystal</td>
<td>34.9</td>
<td>3000</td>
</tr>
</tbody>
</table>

Table 1 Literature results for Magnetic Penetration Depths and $T_C$’s of La$_{1.85}$Sr$_{0.15}$CuO$_4$

4.2 Samples

The thin films of LSCO were made by pulsed laser deposition by the Rutgers University group. Four films around 1000 Å thick were grown, and in an attempt to reduce the effects of strain in the films, five films were grown with thicknesses from
Figure 13. $\lambda(0)$ for La$_{2−x}$Sr$_x$CuO$_4$ as a function of Sr doping, $x$, from the literature. The data from Jaccard et al. were measured in films and have the largest values for $\lambda(0)$ while the rest of the data are from bulk samples.
In all of the films, $\lambda$ is greater than the film thickness, so the measurement probes the entire thickness of the film. The films were grown on either 5 mm or 7 mm square LaSrAl$_2$O$_3$ substrates, which have an excellent lattice match to the films. Three of the films, LA, LB1, and LC1, were post annealed at 400'C in 70 bars of O$_2$ in an attempt to increase their oxygen concentration. The anneal increased $T_C$ by a few degrees.

The resistivities of the post annealed films are shown in Figure 14. The films were patterned into 4 mm by 2 mm strips for resistivity measurements, which were made after the mutual inductance measurements. Their resistivities at 300 K are twice as large as found for bulk LSCO. Takagi et al. report $\rho(300 \text{ K}) = 0.24 \text{ m\Omega cm}$ for $x=0.15$. The residual resistivity indicates higher disorder in films than in crystals. X-ray diffraction of similar films shows excellent c-axis alignment with the substrate and an absence of foreign phases.

4.3 Penetration Depth Results

We have measured the penetration depth in six optimally doped films with nominal Sr concentrations of $x = 0.15$, and $T_C$'s between 20 and 30 K, one underdoped film with $x = 0.135$ and $T_C = 30$ K, and two overdoped films with $x = 0.175$ and $T_C \sim 27$K (Table 2). The reduction in $T_C$ of films compared to bulk samples is commonly attributed in part to strain in the films due to the lattice mismatch with the substrate. The transition temperatures of the optimally doped films increase with film thickness until the thickness is greater than 2000 Å. This is consistent with an increased release of
Figure 14. Resistivity vs. T for LB1 (x = 0.15), LA (x = 0.135), and LC1 (x = 0.175).
strain. Increasing the thickness from 2000 to 6000 Å has no effect on $T_C$, and the highest $T_C$, 31 K, is still lower than the $T_C$'s of optimally doped sintered pellets which is 37 K. In addition to strain, $T_C$ can be reduced by oxygen vacancies which could account for some of the suppression in $T_C$ of the thicker films. Oxygen vacancies can reduce the superfluid density by reducing the normal state carrier density below optimal doping, and by introducing disorder. It is interesting to note that the shortest penetration depth, i.e., the largest superfluid density, is in the optimally doped film that was post-annealed in high pressure oxygen.

<table>
<thead>
<tr>
<th>Film Name</th>
<th>“x” in $La_{2-x}Sr_xCuO_4$</th>
<th>$T_C$ (K)</th>
<th>$\lambda(4K)$ (Å)</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA</td>
<td>0.135</td>
<td>31 ± 1</td>
<td>5900 ± 300</td>
<td>3600</td>
</tr>
<tr>
<td>LB1</td>
<td>0.15</td>
<td>30.5 ± 0.4</td>
<td>4500 ± 300</td>
<td>2700</td>
</tr>
<tr>
<td>LB2</td>
<td>0.15</td>
<td>27.5 ± 0.4</td>
<td>6000 ± 2000</td>
<td>5000</td>
</tr>
<tr>
<td>LB3</td>
<td>0.15</td>
<td>25-30 ± 3</td>
<td>6600 ± 500</td>
<td>1200</td>
</tr>
<tr>
<td>LB4</td>
<td>0.15</td>
<td>27 ± 1</td>
<td>7400 ± 500</td>
<td>1120</td>
</tr>
<tr>
<td>LB5</td>
<td>0.15</td>
<td>23 ± 1</td>
<td>7600 ± 500</td>
<td>1200</td>
</tr>
<tr>
<td>LB6</td>
<td>0.15</td>
<td>25 ± 1</td>
<td>8400 ± 500</td>
<td>900</td>
</tr>
<tr>
<td>LC1</td>
<td>0.175</td>
<td>20-27 ± 3</td>
<td>6000 ± 300</td>
<td>3400</td>
</tr>
<tr>
<td>LC2</td>
<td>0.175</td>
<td>27.5 ± 0.4</td>
<td>7000 ± 2000</td>
<td>5000</td>
</tr>
</tbody>
</table>

Table 2. Summary of samples reported in this paper. Sr concentrations are nominal. Thicknesses are calculated from the number of laser shots.

The temperature dependence of $1/\lambda^2$ is shown in Figure 15. Although there is a muddled collection of curves for the nine films, two different functional forms for $1/\lambda^2(T)$ emerge when $1/\lambda^2(T)$ and $T$ for different data sets are normalized such that the data sets intersect at 60% and 90% of “$T_C$” (Figure 16). If $\lambda^2(0)/\lambda^2(T/T_C)$ were a unique
Figure 15. $1/\lambda^2(T)$ vs. $T$ for all nine LSCO films in this study. The labels for the curves are arranged in order of decreasing superfluid density at 1K.
Figure 16. $1/\lambda^2(T)$ vs. $T$, normalized so that the data agree at 0.9 $T_c$ and 0.6 $T_c$. The axis on the right has been shifted for clarity and is valid for the upper set of data. The upper data sets are for films LA, LB1, LB4, LB6, and LC1. The lower data sets are for films LB2, LB3, LB5, LC2. The data clearly show two functional forms.
function of \( T/T_C \), as is approximately true for BCS superconductors with similar levels of disorder, then normalization at any two points would cause the data for all samples to overlap everywhere. We use an unfamiliar normalization scheme, instead of the usual normalization to \( \lambda^2(0) \) and \( T_C \), to allow for different low T behaviors which are expected in d-wave superconductors with different levels of disorder. Some films show a stronger T dependence below 0.5 \( T_C \). The variation in T dependence is not correlated with film thickness, \( \lambda(0) \), \( T_C \), or oxygen post-annealing. The key results of this study are independent of this variation.

The narrowest transitions are less than 1 K wide, such as in LB2 and LC2, while other samples like LC1 and LB3 show very distinct multiple transitions near \( T_C \). Figure 17 illustrates this point with data for \( \sigma_1(T) \) for two films near \( T_C \). The peaks in \( \sigma_1 \) indicate the temperature and width of each transition. While there is some variation in behavior near \( T_C \) among the films, the overall quality of the transitions is good. We suspect that the behavior near \( T_C \) simply indicates a spread in \( T_C \)'s of different layers of the film, due to small changes in deposition parameters during deposition. For \( T \ll T_C \), the order parameter in all layers should be well developed and nearly equal, and since the T-dependence of \( \lambda \) is determined only by the low-energy behavior of the density of states, the small spread in \( T_C \) should not affect \( \lambda(T) \).

A central result of this study is that \( \lambda^2(T) - \lambda^2(0) \) is quadratic in T for all films, regardless of the width of the transition, film thickness, \( T_C \), etc. Figure 18 shows
Figure 17. Real part of the conductivity, $\sigma_1$, vs. $T$ near $T_c$. $\sigma_1$ is shown for a film with multiple transitions, LC1, and a clean transition, LC2. There are no data shown for LC2 below 25.5 K because the average conductivity is zero but extremely noisy. The dissipation for LC1 extends down to at least 23 K.
quadratic fits to the data for films LA, LB1, and LC1. We show these three films since they have the largest superfluid densities for their respective Sr concentrations, and their sample dimensions provided the most accuracy in measuring their superfluid density. The quadratic fits are excellent with the difference between the fit and the data less than ± 1%. A quadratic fits better than an exponential down to the lowest temperature measured. Figure 19 shows an exponential fit for an isotropic s-wave with the temperature dependence as given in equation 2. The values as determined from the fits for 2Δ(0)/kTC are 2.6, 2.4, 2.2 for films LB1, LA, and LC1 respectively. Over the same temperature range that the quadratic fit error is within ± 1% the isotropic s-wave error is greater than ± 2%. For comparison, we also fit the data to an approximated temperature dependence for an anisotropic s-wave by allowing the constant in front of the exponential term to vary as well as Δ.

$$\frac{\lambda^2(0)}{\lambda^2(T)} = 1 - a\sqrt{\frac{2\pi \Delta}{k^* T}} e^{\frac{-\Delta}{k^* T}}$$

(7)

This fit is shown in Figure 20 The parameters for this fit are 2Δ(0)/kTC = 1.6, 1.4, 1.2 and a = 0.364, 0.274, 0.36 for LB1, LA, LC1 respectively. The anisotropic fit is clearly an improvement on the isotropic fit, but the fit is poorest at the lowest temperatures where we are looking for the best fit. If an exponential temperature dependence exists in these samples it would have to do so below our measurement range. Over the range of 2 K to 8 K these data have a quadratic temperature dependence. Given that the resistivity
Figure 18. Quadratic fits to $\lambda^{-2}(T)$ below 10 K. Data are shown for films LB1 ($x = 0.15$), LA ($x = 0.135$), and LC1 ($x = 0.175$). The lower curve shows the % difference between the fit and the data.
Figure 19. Exponential fits to $\lambda^{-2}(T)$ below 10 K. Data are shown for films LB1 ($x = 0.15$), LA ($x = 0.135$), and LC1 ($x = 0.175$) with a best fit to the temperature dependence from a BCS isotropic s-wave density of states. The lower curve shows the % difference between the fit and the data.
Figure 20. Exponential fits to $\lambda^{-2}(T)$ below 10 K. Data are shown for films LB1 ($x = 0.15$), LA ($x = 0.135$), and LCI ($x = 0.175$) with a best fit to the temperature dependence from an anisotropic s-wave density of states. The lower curve shows the % difference between the fit and the data.
data indicate a substantial level of disorder in films, and given the strong support for
d-wave superconductivity in YBCO, also a hole-doped cuprate, these data strongly
support the conclusion that LSCO is a d-wave superconductor. Moreover, as discussed
below, the substantial increase in \( \lambda(0) \) in thin films relative to bulk samples is more
consistent with d-wave than with s-wave superconductivity in this compound.

We cannot categorically rule out some sort of unusual s-wave state, but we can
put severe limits on it. It is possible that the data would become exponential below 2 K,
so that we can only put an upper limit of about 20 K on the minimum isotropic energy
gap. This limit gives \( 2\Delta(0)/kT_c < 1.3 \), much smaller than the value of 3.53 found in weak-
coupling BCS superconductors.

We can further constrain the possible s-wave states by considering the effects of
disorder on the minimum gap. If disorder in the films relative to bulk samples is
nonmagnetic, it would cause an anisotropic s-wave state in the hypothetical pure material
to become isotropic with \( 2\Delta(0)/kT_c \) close to the BCS value\(^{62}\) which is clearly not
observed. Of course, some of the disorder may be magnetic in nature. According to
theory, if the roughly 20\% (7 K) suppression of \( T_C \) in the highest \( T_C \) films relative to bulk
samples was all due to magnetic impurities in an isotropic s-wave superconductor, then
the energy gap \( \Delta \) in the density of states would be about 40 K in the films.\(^{63}\) If other
mechanisms, such as strain, are causing some of the decrease in \( T_C \) then \( \Delta \) would be larger
than 40 K. Therefore magnetic impurities in an isotropic s-wave state is not a likely
candidate for LSCO. Given the effects of disorder on the temperature dependence of an
anisotropic s-wave order parameter, the observed temperature dependence is inconsistent
with an anisotropic order parameter with nonmagnetic impurities or an isotropic order parameter with magnetic impurities.

The magnitude of $\lambda(0)$ in these films is much larger than the value of $\lambda(0)$ reported for crystals and sintered pellets which is $2500 \pm 400$ Å. The convenient quantity for comparison with $d$- and $s$-wave models is the superfluid density, $n_s(0) \propto \lambda^{-2}(0)$. Among our films, $n_s(0)$ is smaller than in bulk materials by a factor of 4 to 10. In a $d$-wave interpretation, this is a natural consequence of disorder competing with an anisotropic gap which cannot be made isotropic by disorder. In $s$-wave superconductors, it would indicate that the mean free path, $\ell$, has dropped to one fourth to one tenth of the GL coherence length, which would put $\ell$ somewhere below 4 Å which is quite unreasonable. There is no peak in the resistivity above $T_C$ which would indicate that the disorder is causing strong localization of electrons, and thereby reducing $n_s$. A second explanation for a decrease in the superfluid density in an $s$-wave state is magnetic scattering. In this case for a suppression in $T_C$ of 20%, theory predicts a suppression in $n_s$ of about 20%, also. Obviously, this is much smaller than the factor of 4 to 10 which is observed. In short, a $d$-wave interpretation accounts for the suppression in $n_s$ much more naturally than an $s$-wave interpretation.

The only problem with the $d$-wave interpretation is the same problem encountered in studies of YBCO films deliberately disordered by chemical substitutions on the Cu site, namely, the suppression in $n_s(0)$ is larger than expected from the suppression in $T_C$. Within the simplest weak-coupling $d$-wave picture, one must conclude that disorder actually strengthens the mechanism for superconductivity, making superconductivity more
robust than expected against scattering rates larger than the measured $T_C$ of the clean compound. Including strong coupling in the theory tends to improve agreement, but this remains an open issue.

4.4 Conclusion

The characteristic features of our data on $\lambda(T)$ in LSCO films are explained in terms of a $d$-wave superconducting order parameter including disorder generated during the film fabrication. These features include the increased $\lambda(0)$'s, increased resistivities, and the suppressed $T_C$'s of films relative to bulk, and the quadratic $T$-dependence of $\lambda^2(T)$ - $\lambda^2(0)$ at low $T$. These features are shared with YBCO films deliberately disordered by chemical substitutions. Explanations of the data in terms of simple $s$-wave superconductivity, namely, a reduced electron mean free path or magnetic scattering, were found to be unlikely. Given the similarities in the structure and hole-like normal-state electronic behavior of the CuO planes in YBCO and LSCO, and the similarities in the behavior of $\lambda(T)$ in doped YBCO and in LSCO films, the natural conclusion is that they share the same order parameter symmetry.
CHAPTER 5

YBCO SUPERCONDUCTING- NORMAL TRANSITION, CRITICAL REGION

5.1 Introduction

A thorough understanding of the role of thermal fluctuations is central to the advancement of a workable model of high temperature superconductivity. Thermal fluctuations of the order parameter are pervasive, and influence essentially all measurable parameters including the superfluid density, specific heat, complex conductivity, and magnetization. Near the superconducting-to-normal transition where the order parameter becomes vanishingly small, fluctuations are expected to play a prominent role. In addition, it is has been proposed that thermal fluctuations play a substantial role at temperatures well away from the transition, causing significant deviations from mean-field (MF) calculations.\cite{64,65,66} It is predicted that thermal phase fluctuations will impress a linear-in-T dependence upon the superfluid density, \( n_s \sim \lambda^2(T) \), at low temperatures. Such a contribution may effectively mask a crossover to BCS like behavior that may be induced by substantial chemical or radiation damage.

Near the transition, the temperature range over which fluctuations dominate the behavior of the properties of the material is known as the critical region. The width of the
critical region serves as a measure of the strength of fluctuations. The influence of low
temperature fluctuations can be estimated by the measured strength of fluctuations near
the transition. The large penetration depths $\lambda$ and short coherence lengths $\xi$ of high
temperature superconductors suggest a significant enhancement of fluctuations relative to
low $T_c$ superconductors

In applied magnetic fields of 1-5 Tesla, the critical region is clearly observed in
YBCO and it is well described by the 3D $XY$ model. Studies of critical dynamics in
applied fields include measurements of heat capacity, magnetization, and I-V
characteristics. All of these properties are found to obey power laws and scaling
functions consistent with a 3D $XY$ critical region several degrees wide. However, there is,
no clear sense of the exact manner in which the critical region width varies as a function of
the field magnitude. For fields below 1 Tesla scaling arguments work poorly indicating
that fluctuations must become less significant with decreasing field. Above 5 Tesla
multicritical scaling becomes important as 3D $XY$ behavior merges with the glassy vortex
dynamics and lowest Landau level behavior which dominate at high fields.

In addition to the possibility that a magnetic field affects the width of the critical
region, it is also possible that the universality class of the critical region is changed by the
presence of a field. Therefore, zero field measurements of critical behavior are a necessary
step towards a complete understanding of thermal fluctuations. Published zero field
measurements of specific heat and I-V characteristics are inconclusive regarding the width
and universality class of the critical region. Though there have been measurements
of the specific heat both in zero and non-zero magnetic fields, the zero field results
provide no clear indication of critical behavior. DC and AC conductivity measurements above \( T_C \) can be fit assuming Gaussian fluctuations to within 0.6 K of \( T_C \). This result constrains the critical region to less than 0.6 K above \( T_C \); however, it is not clear that fluctuation effects are necessarily symmetrical about \( T_C \). The magnetic penetration depth can be used to probe fluctuation effects below \( T_C \).

The penetration depth serves as a powerful tool in determining the presence or absence of critical behavior for two reasons. First, the penetration depth has no normal state analog, and therefore, no background corrections are necessary as is the case with measurements of the conductivity and specific heat. Second, the inverse squared penetration depth is directly related to the superconducting order parameter (\( 1/\lambda^2 \sim |\psi|^2 \sim n_s \)) and therefore provides directly identifiable distinctions between MF and critical behavior. The MF temperature dependence of the superfluid density \( n_s \) is linear in \( T \), \( n_s \sim (T_C - T) \). Near the transition, fluctuations become significant such that \( n_s \) is suppressed and will behave according to a particular universality class, most often assumed to be 3D \( XY \). According to the 3D \( XY \) model, \( 1/\lambda^2 \sim (T_C - T)^{2/3} \). Thus, by determining the power law behavior of the superfluid density as \( T \) approaches \( T_C \), it is possible to distinguish critical from MF behavior and set an upper bound on the width of the critical region.

Previous studies of the critical region based on measurements of the magnetic penetration depth are contradictory. Kamal \textit{et al.}\textsuperscript{17} and Anlage \textit{et al.}\textsuperscript{18} both report a 2/3 power law behavior over 10 K and 3 K respectively. These results seem to indicate that the critical region is quite large, exceeding the predictions of the Ginzburg criterion by a factor of 10 or more. In contrast, Lemberger \textit{et al.}\textsuperscript{47} and Goldman \textit{et al.}\textsuperscript{77} have published
results showing linear behavior of $1/\lambda^2$ in films which are consistent with a critical region no wider than 1 K. It has been argued that the MF results are associated with defects inherent in thin films since critical regions larger than 1 K have been reported only in single crystals. Intuitively, however, we expect that the increased defect density associated with films would cause an enhancement of fluctuations leading to a wider, not narrower, critical range. Recently, data taken by Harihanan et al.\textsuperscript{78} indicate a narrow critical region in high purity crystals corroborating the MF results seen in films. We examine the magnetic penetration depth in several samples made by three different growth techniques to clarify the extent of the critical region below $T_C$ in zero field.

5.2 Superfluid Density Near $T_C$

We have studied ten high quality pure YBCO thin films of varying thicknesses made by pulsed laser deposition, sputtering, and co-evaporation. The films measured are between 500 and 2500 Å thick on SrTiO$_3$ substrates which are either 1 cm square or 15 mm circular, and approximately 1 mm thick. Each film growth technique is expected to produce a different microstructure enabling us to compare disorder dependent effects. Even with these various deposition techniques, we note that there could still remain some property, such as epitaxial strain and generally higher defect densities, associated with all film growth techniques which would distinguish them from crystals. The films all have sharp transitions, indicative of good homogeneity, with $T_C$'s ranging from 88 to 91 K. A typical transition width is 0.5 K, and the narrowest transition is less than 0.2 K as determined from the width of the real conductivity peak. The films display low
Figure 21. $\lambda^2(T)$ for all ten YBCO films studied. The films, in order of decreasing superfluid density at 4 K, are YD, YA, YB, YE, YC, YG, YH, YI, YJ, YF. Films YA-YC were made by co-evaporation, films YD-YF were made by sputtering, and films YG-YJ were made by laser ablation.
temperature penetration depths of 1500 - 2500 Å and have well behaved $\lambda(T)$ over the measured temperature range of 4 K to $T_C$ (Figure 21).

<table>
<thead>
<tr>
<th>Film</th>
<th>Thickness (Å)</th>
<th>$\lambda(4,K)$ (Å)</th>
<th>$T_C$ (K) ± 0.1K</th>
<th>$\Delta T_C$ (K)</th>
<th>$2\beta_{P(T)}$ from $P(T)$ ± 0.05</th>
<th>Range of $2\beta$ from $P(T)$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YA</td>
<td>1000 ± 100</td>
<td>1680 ± 100</td>
<td>90.5</td>
<td>0.8</td>
<td>0.90 ± 0.05</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>YB</td>
<td>1000 ± 100</td>
<td>1770 ± 100</td>
<td>90.1</td>
<td>0.2</td>
<td>0.95 ± 0.05</td>
<td>3 ± 1</td>
</tr>
<tr>
<td>YC</td>
<td>1000 ± 100</td>
<td>1880 ± 100</td>
<td>89.6</td>
<td>1</td>
<td>1.02 ± 0.05</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>YD</td>
<td>750 ± 100</td>
<td>1520 ± 150</td>
<td>88.2</td>
<td>0.2</td>
<td>0.98 ± 0.05</td>
<td>3 ± 1</td>
</tr>
<tr>
<td>YE</td>
<td>600 ± 100</td>
<td>1730 ± 150</td>
<td>88.4</td>
<td>1.3</td>
<td>1.03 ± 0.05</td>
<td>3 ± 1</td>
</tr>
<tr>
<td>YF</td>
<td>1100 ± 100</td>
<td>2390 ± 100</td>
<td>88.8</td>
<td>0.5</td>
<td>0.80 ± 0.05</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>YG</td>
<td>500 ± 50</td>
<td>1940 ± 150</td>
<td>89.8</td>
<td>0.2</td>
<td>0.78 ± 0.05</td>
<td>1.5 ± 0.5</td>
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<tr>
<td>YH</td>
<td>1500 ± 150</td>
<td>2110 ± 150</td>
<td>90.5</td>
<td>0.4</td>
<td>0.93 ± 0.05</td>
<td>3 ± 1</td>
</tr>
<tr>
<td>YI</td>
<td>500 ± 50</td>
<td>2110 ± 150</td>
<td>89.4</td>
<td>0.4</td>
<td>0.87 ± 0.05</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>YJ</td>
<td>1500 ± 150</td>
<td>2180 ± 150</td>
<td>89.9</td>
<td>0.4</td>
<td>0.78 ± 0.05</td>
<td>0.5 ± 0.5</td>
</tr>
</tbody>
</table>

Table 3. Parameters of pure YBCO films studied.

We focus now on $\lambda^2(T)$ vs. $T$ near $T_C$. To make a general qualitative comparison of all of the films in the transition region, we normalize $T$ to $T_C$ and $\lambda^2(T)$ to $\lambda^2(0.96T_C)$, as is shown in Figure 22. The behaviors of all of the films are in good agreement from 0.96 $T_C$ to 0.99 $T_C$. Although all of these samples are subject to defects inherent to films, the exceptional agreement over such a broad temperature range for films made by three
Figure 22. $\lambda^2(T)$ for all ten films normalized in temperature to $T_c$ and in penetration depth to $\lambda^2(0.96 \ T_c)$. All of the films show similar behavior in the range $0.96T_c < T < 0.99T_c$ and appear to be close to linear-in-$T$. Sample-to-sample variations become evident only within 1 K of $T_c$. 
different growth techniques leads us to believe that this behavior is representative of continuous films.

Above 0.99 $T_c$, behavior is sample dependent. There are several plausible explanations for this behavior. The most likely interpretation is that the films which show a drop in superfluid density do so as a result of grains with various values of $T_c$ which leads to percolative behavior. These observed drops in the superfluid density are reminiscent of a KT transition except the location of the drop is inconsistent with KT theory as given in equation 6. An upward curvature in $n_s$ probably stems from slight variations in $T_c$ through the film thickness due to slight variations in deposition conditions during film growth. Given that the variation in behavior from sample to sample is evident only in this region, we presume that disorder effects do not play a significant role in determining behavior in the region $0.96 T_c < T < 0.99 T_c$.

For each film we make a detailed quantitative analysis. To determine the existence of a critical exponent we define the function $P(T)$,

$$P(T) = \frac{\lambda^2(T)}{\partial \lambda^2 / \partial T}. \quad (8)$$

Both $\lambda^2$ and $\partial \lambda^2 / \partial T$ are determined from the data. If $\lambda^2(T) \sim (T_c - T)^{2\beta}$ then we would observe:

$$P(T) = \frac{1}{2\beta} (T - T_c). \quad (9)$$

61
A linear, least squares fit to \( P(T) \) yields both \( T_c \) and the value for the exponent \( \beta \). For universal critical behavior, the slope, \( 1/2\beta \), will be identical from film to film with a value \( 2\beta = 0.67 \) for the 3D XY universality class.

Figure 23 shows \( P(T) \) for the three co-evaporated films. The dashed line in Figure 23 indicates 3D XY behavior, demonstrating that 3D XY behavior is outside of experimental uncertainty. The least squares fit over the temperature range from \( 0.96T_c \) to about \( 0.995T_c \) gives values of \( 2\beta = 1.02, 0.95 \) and \( 0.90 \) for films YA, YB, and YC respectively. In the sample with the sharpest transition, YB, there is no significant deviation from MF behavior, \( 2\beta = 1 \), to within 0.2 K of a vanishing superfluid density.

Figure 24 shows \( P(T) \) for the three sputtered films. The least squares fit over the temperature range from \( 0.96T_c \) to about \( 0.99T_c \) gives values of \( 2\beta = 0.98, 0.80 \), and 1.03 for films YD, YF, and YE respectively. Figure 25 shows \( P(T) \) for the four laser ablated films. The least squares fit over the temperature range from \( 0.96T_c \) to about \( 0.99T_c \) gives values of \( 2\beta = 0.87, 0.93, 0.78 \), and 0.78 for films YI, YH, YG, YJ, respectively. In film YG, the range of temperatures over which \( P(T) \) is linear is relatively short and \( P(T) \) for film YG does not seem to be truly linear over any range. Yet for none of the films is the value of \( 2\beta \) close to the 3D XY value of 0.67. Since MF behavior is observed in most of the films to within 0.5 K of \( T_c \), we set 0.5 K as an experimental upper bound on the width of the critical region in YBCO films. The film with the narrowest transition suggests that the intrinsic critical region may be smaller than 0.2 K. There does not exist any monotonic correlation between the magnitude of \( \lambda(0) \) and the measured exponent which leads us to conclude that the range of values found for the exponent are simply
Figure 23. \( P(T) = \frac{1}{\lambda^2} \) is shown for the three co-evaporated films YC, YB, YA. Linear least squares fits yielding the temperature exponents \( 2\beta = 1.02, 0.95 \) and 0.90 respectively are shown as solid lines. The dashed line represents the linear behavior expected of a 3D \( XY \) exponent \( 2\beta = 0.67 \).
Figure 24. $P(T) = \frac{1/\lambda^2}{\partial(1/\lambda^2)/\partial T}$ is shown for the three sputtered films YD, YF, and YE. Linear least squares fits yielding the temperature exponents $2\beta = 0.98$, $0.80$, and $1.03$ respectively are shown as solid lines.
Figure 25. $P(T) = \frac{1/\lambda^2}{\partial(1/\lambda^2)/\partial T}$ is shown for the four laser ablated YI, YH, YG, and YJ. Linear least squares fits yielding the temperature exponents $2\beta = 0.87, 0.93, 0.78, \text{ and } 0.78$ respectively are shown as solid lines.
variations in "mean-field" behavior associated with slight variations in film parameters and microstructure.

For comparison we can also look for a critical region in LSCO. The large penetration depths in LSCO films relative to $\lambda(0)$ in YBCO are expected to result in a critical region which is at least as wide as in YBCO. In films LB2 and LC2, $\lambda^{-2}$ is the same function of $T/T_C$ near $T_C$, as shown in Figure 26, and the transition is about 0.8 K wide as measured by the FWHM of the peak in $\sigma_I$. These are the two LSCO films with the sharpest transitions, and it is clear that 3D $XY$ behavior does not occur (Figure 26). In fact, $1/\lambda^2$ curves slightly upward, rather than sharply downward, as T approaches $T_C$. The upward curvature is indicative of a spread in $T_C$'s throughout the layers of the film. The critical region is less than 1 K wide as determined from the highest temperature of the linear portion of the $1/\lambda^2$ data. The upper bound on the critical range is large due to the width of these transitions. We note that Jaccard et al. concluded that the critical region is about 2 K wide in their LSCO films.

Let us consider how properties inherent to YBCO films may or may not affect the observed results with respect to the 3D $XY$ behavior reported in YBCO crystals. In general, we expect that defects inherent in films, such as grain boundaries, to enhance fluctuations. In a film where grain boundaries dominate the sheet inductance we expect an even more dramatic suppression in the superfluid density than the $2\beta = 0.67$ behavior of 3D $XY$. Microscopic defects such as dislocations or twins would nucleate extra fluctuations not found in crystalline samples. Moreover, given the fact that some of our films have $\lambda(0)$ significantly larger than the 1400 Å value associated with clean crystals,
Figure 26. $1/\lambda^2$ vs. $T$ for films LB2 and LC2 near $T_c$. 
the Ginzburg criterion leads us to expect fluctuations to be stronger in films. The recent work of Harihanan et al.\textsuperscript{8} confirms that high purity crystals can exhibit a narrow critical range as well. It is plausible that the rapid decrease in quasiparticle scattering rate just below $T_c$ observed in microwave cavity measurements on crystals\textsuperscript{80} might impress an extra temperature dependence on the superfluid density since the superfluid density should be sensitive to the quasiparticle mean free path. Such a rapid decrease is not observed in films, and its absence is ascribed to the effects of weak disorder on a d-wave superconducting order parameter.

We acknowledge the importance of keeping measurements of $\lambda(T)$ within the linear-response regime. To illustrate this point, we have performed our experiment outside of the linear response regime. Two sets of $\lambda^2(T)$ data taken on the film YB, one set in the linear response regime and another out of the linear response regime, are shown in the inset of Figure 27. The data taken at low current are linear to within 0.2 K of the transition. Data taken in the nonlinear response regime begin to show a significant suppression in the superfluid density at about 88 K, and are reminiscent of the shape expected from 3D $XY$ behavior. We fit $P(T)$ for the non-linear regime data from 88.0 to 89.4 K, the region that appears to the eye to behave as 3D $XY$. Figure 27 shows $P(T)$ for the high current data and the best fit, yielding $2\beta = 0.70$, which is quite close to the 3D $XY$ value $2\beta = 0.67$. Use of too high a current would lead to an erroneous identification of a critical region 1.4 K wide, an order of magnitude larger than the critical region width of less than 0.2 K. In the nonlinear response regime both the width of the critical region and the value of the exponent are sensitive to the magnitude of the induced supercurrent.
Figure 27. $P(T)$ for film YB taken in the nonlinear response range. The superfluid density is artificially suppressed, increasing the curvature in $\lambda^2(T)$. A linear least squares fit yields an exponent $2\beta = 0.70$, close to the expected 3D $XY$ result. The inset shows $\lambda^2(T)$ measured both in the linear, 1 mA, and nonlinear, 17 mA, response regimes.
We emphasize again that great care has been taken to ensure that our measurements were performed in the linear response regime to within 0.05 K of $T_c$.

5.3 Conclusion

There is no evidence for a large critical region in YBCO from the magnetic penetration depth measured in samples made by sputtering, co-evaporation and pulsed laser deposition. The critical region in YBCO is less than 0.5 K wide in all of our films. Based on the results of our film with the sharpest transition, we conclude that an intrinsic critical region will be less than 0.2 K wide. In LSCO, the upper bound for the critical region is 1 K which is a limited by the spread in $T_c$ of the samples we studied. The upper bounds on the range of critical behavior in YBCO is consistent with the typical Ginzburg criterion estimate. A small critical region indicates that fluctuations do not play as significant a role in YBCO as might be presumed.
APPENDIX A

COMPARISON OF CHAIN AND PLANE DOPANTS IN YBCO

The purpose of this study was to compare the effects of plane and chain doping on YBa$_2$Cu$_3$O$_{7.5}$. Plane dopants were expected and found to have a larger effect on the superconducting transport properties than chain dopants.

The films in this study are 300 nm thick, made by laser ablation on SrTiO$_3$ substrates. The samples are about 1.5 cm in radius. They are highly oriented with the c axis perpendicular to the substrates. Cobalt substitutes exclusively for the chain coppers while Zn substitutes preferentially for the plane coppers in YBa$_2$Cu$_3$O$_{7.5}$. $^8$ $T_c = 72$ K for the 3% Co film and $T_c = 43$ K for the 4% film.

Figure 28 shows a comparison of the infrared reflectances of a 3% Co doped and 4% Zn doped YBa$_2$Cu$_3$O$_{7.5}$ film measured at 10 K, 100 K, and 300 K. The strong features in the spectra at 86 cm$^{-1}$, 176 cm$^{-1}$, and 550 cm$^{-1}$ are from phonons in the substrate. The infrared reflectance spectra of the 3% Co and the 4% Zn doped sample are nearly indistinguishable at 300 K. This result implies that the normal state properties, such as the Drude scattering rate and the plasma frequency averaged over the a-b plane of our
twinned samples, are the same for the chain and the plane doped samples. At 100 K the 3% Co and 4% Zn reflectance spectra are both higher and still similar to each other.

In the superconducting state the spectra of the 3% Co and the 4% Zn doped samples are quite different. The reflectance of the 4% Zn sample is higher at 10 K than at 100 K but it is not close to unity, and therefore the sample is "gapless". Kim et al. have fit the 10 K reflectance data with a mid-infrared band and a Drude conductivity which has no missing area. They get a better fit by using a modified Drude conductivity with missing area corresponding to the measured penetration depth. In contrast, the 3% Co sample has a much higher reflectance at 10 K than at 100 K. In fact it goes to unity at low frequency within experimental error. The higher reflectance is consistent with the much smaller penetration depth of the 3% Co film compared to that of the 4% Zn film. The 10 K spectrum of the 3% doped sample is qualitatively similar to that of pure YBa$_2$Cu$_3$O$_{7.5}$. At low frequencies, both the pure and Co doped YBa$_2$Cu$_3$O$_{7.5}$ have a reflectance near unity. The reflectances decrease with increasing frequency and have a shoulder which occurs near 230 cm$^{-1}$ in the spectrum of the Co doped sample. Although the normal state properties of the two samples are the same, the superconducting properties of the plane doped samples are suppressed to a greater extent than those of the chain doped sample.

The magnetic penetration depth, $\lambda(T)$, was measured by the two coil method. The sharpness of the transition in the mutual inductance, shown in the inset to Figure 29, indicates that the Co is evenly distributed throughout the sample, since $T_C$ is very sensitive to Co doping. With 2% Co, $T_C = 91.5$K, but with 3% Co $T_C = 72$ K so a
Figure 28. Reflectance of $\text{YBa}_2(\text{Cu}_{0.97}\text{Co}_{0.03})_3\text{O}_{7.5}$ and $\text{YBa}_2(\text{Cu}_{0.97}\text{Zn}_{0.04})_3\text{O}_{7.5}$ films at 10K, 100 K, and 300K. The thick lines are the Co doped sample and the thinner lines are the Zn doped sample. Note that the 300K reflectance spectra for the Co and Zn doped samples are the same while their 10K reflectance spectra are very different. The 10 K reflectance for the Co goes to unity, but the 10K Zn reflectance stays low. The data have been smoothed for clarity.
Figure 29. $1/\lambda^2$ (T) for a YBa$_2$(Cu$_{0.97}$Co$_{0.03}$)$_3$O$_{7.8}$ and YBa$_2$(Cu$_{0.97}$Zn$_{0.04}$)$_3$O$_{7.5}$ film. Note that $1/\lambda^2$ for the 3% Co film is much higher than $1/\lambda^2$ for the 4% Zn doped film. For comparison, pure films have $1/\lambda^2(4K) = 40 \mu m^{-2}$. The inset shows the mutual inductance as a function of temperature for the Co doped sample.
spread in concentration between 2.5 and 3%, for example, would lead to a 10-20 K transition width.

Figure 29 is a comparison of the temperature dependence of $1/\lambda^2$ for the 3% Co and 4% Zn doped samples. The penetration depth at 4 K for the 3% Co sample is 210 nm ± 15 nm which is about 40% larger than that of pure YBa$_2$Cu$_3$O$_{7.4}$ films where $\lambda$ (4 K) = 150 - 170 nm. The penetration depth, $\lambda$ (4 K) = 750 nm ± 80 nm, for the 4% Zn doped sample is much larger than pure or Co doped YBa$_2$Cu$_3$O$_{7.8}$. The superfluid density which is proportional to $1/\lambda^2$ is only decreased by a factor of two between the pure film and the 3% Co doped film while it is decreased by a factor of 25 between the pure film and the 4% Zn film.

In the chain-doped sample the superconducting properties are not greatly altered from the pure samples, while the plane-doped sample the superconducting properties are altered. 3%Co doped YBa$_2$Cu$_3$O$_{7.8}$ has a penetration depth and an infrared reflectance at 10 K similar to pure YBa$_2$Cu$_3$O$_{7.8}$. 4% Zn doped YBa$_2$Cu$_3$O$_{7.8}$ has a much larger penetration depth than pure YBa$_2$Cu$_3$O$_{7.8}$ and a gapless reflectance.
APPENDIX B

OXYGEN DEPLETED YBCO

YBCO is different from other cuprates in that it has both Cu-O planes and Cu-O chains. A complete understanding of the material must include the role of these different layers. It is a subject of debate as to what extent there is superconductivity in the chain layers. One theory is that the chains and the planes each have an s-wave order parameter which when taken together appear d-wave in nature. Oxygen depletion reduces the carrier concentration and adds disorder to the chain layers. By studying the effects of oxygen depletion on the superfluid density we can discern the role of the chains in the superconductivity of YBCO.

It is possible to vary the oxygen concentration in YBCO from 6.0 - 7.0. Around 6.5 YBCO undergoes an orthorhombic to tetragonal transition in the crystal structure. At approximately the same oxygen concentration the $T_C$ of YBCO goes to zero. The optimal oxygen concentration is 6.95. For small reductions in the oxygen concentration there is little shift in $T_C$. With further oxygen depletion $T_C$ is steadily reduced to about 60K where there is a plateau in $T_C$ vs. $\delta$. The plateau is a result of the oxygen in the chains ordering.
around half filling. The oxygens order into alternating chains. For further reduction in oxygen \( T_c \) falls rapidly to zero.

Sample Preparation

The deoxygenation was carried out in a quartz tube furnace. The tube furnace was evacuated to 60 mTorr and flushed with Ar. This was repeated three times while the tube furnace was heated to 250 K. While Ar gas was flowing through the tube furnace the samples was slid into the center of the tube furnace. After a dwell of between 5 and 10 min, the sample was slid to the cool end of the furnace. The short anneal time and low anneal temperature ensures that only the oxygen concentration is changed.

The penetration depth is measured with a two coil mutual inductance technique that has been continuously improved. The three samples originally studied by Lee et al.\(^4\) were measured with an earlier probe in which only the change in \( \lambda(T) \) was determined absolutely. A functional form for \( \lambda(T) \) was assumed for determining the calibration constant. Although choosing the wrong \( \lambda(T) \) does not affect \( \lambda(0) - \lambda(T) \), it does affect the calculated \( \lambda(0) \). The technique has since been improved so that the calibration constant is determined experimentally and the absolute value of \( \lambda \) can be determined accurately. In this study one additional film (D) was measured at various oxygen concentrations and one of Lee et al.'s films (B) was remeasured in its final deoxygenated state and then reoxygenated. The measurement of Lee et al.'s films with the new probe validates the previous procedure for determining \( \lambda(0) \).
Figure 30. $T_c$ vs. $1/\lambda^2(0)$ For four oxygen depleted films compared to oxygen depleted films of Uemura et al. The filled-in triangles are data for film B which was remeasured a year later with a new probe in its final oxygen state and then reoxygenated.
Figure 31. $1/\lambda^2$ vs. $T$ for the oxygen depleted films, A, B, C, of Lee et al.\textsuperscript{84}
Figure 32. $1/\lambda^2$ vs. $T$ for the 8 oxygen depleted states of film D.
Figure 30 is a comparison of the results of Lee et al.\textsuperscript{84} with a new film measured with the improved probe. Data from \textmu sSr measurements on oxygen depleted crystals by Uemura et al. are also shown. Film B of Lee et al. was remeasured with the improved probe a year after the initial study. The T\textsubscript{C} of the film had increased by 3 K and the superfluid density had also increased. The increased value of the superfluid density at 4 K agreed with the previous value of the superfluid density with a similar T\textsubscript{C}. This agreement validates the earlier procedure for determining \lambda(T). The increase of T\textsubscript{C} was due either to an uptake of O\textsubscript{2} or a reordering of oxygen. The film was reoxygenated at 450° C in flowing O\textsubscript{2} for 90 min. The T\textsubscript{C} increased to 84 K.

There are two plateaus in T\textsubscript{C} vs. 1/\lambda\textsuperscript{2}. The 90 K plateau and the 60 K plateau are at the location of the plateaus in T\textsubscript{C} vs. \delta. The overall shape of T\textsubscript{C} vs. n\textsubscript{c} is reminiscent of T\textsubscript{C} vs. \delta and indicates that the carrier density is proportional to \delta. The data of Lee et al.\textsuperscript{84} is consistent with the new measurement of film D.

The temperature dependence of 1/\lambda is shown in Figure 31 for the films of Lee et al. The superfluid density of the films are quadratic at low temperatures as is true for a disordered d wave. The temperature dependence of the superfluid density is unchanged with oxygen depletion except in the transition region. The difference in the transition region is most likely due to some inhomogeneity in the oxygen concentration through the thickness of the film. Film D has similar results to films A, B, and C in that the temperature dependence remains unchanged with oxygen depletion although it had an unusual temperature dependence in the as-made state (Figure 32). Figure 33 shows the
Figure 33. $\lambda^2(0)/\lambda^2(T)$ vs. $T/T_C$ for film D with different O stoichiometry.
data for film D normalized to $T_C$ and $\lambda^2(0)$. The temperature dependence for low $T$ is the same for all of the oxygen states. The behavior of $1/\lambda^2(T)$ in the transition region changes with lower oxygen concentration due to inhomogeneity of the oxygen.

Conclusion

The primary effect of oxygenation is to change the carrier concentration in YBCO. Since the increased scattering in the chain layers of YBCO due to $O_2$ depletion had a minimal effect on the temperature dependence of $\lambda(T)$ it seems likely that the chains are not a major contributor to the superconductivity in YBCO.
APPENDIX C

MAGNETIC PENETRATION DEPTH IN BSCCO

We have measured the magnetic penetration depth in a series of BSSCO films. The low temperature data are analyzed in terms of a d-wave order parameter. In one thin film it is possible to observe individual layers become superconducting.

The BSCCO films were made by molecular beam epitaxy (MBE) with REED technology which permits visualization and control of the individual layer growth. The BSCCO 2212 films were grown on SrTiO₃ substrates with a layer of SrO followed by two layers of BiO and two layers of carrier depleted BSCCO 2201. The 2201 layers are added to provide a better lattice match to the 2212 which should reduce strain in the 2212. In one BSCCO film the 2201 layer is visible at sufficiently low drive current as will be discussed later.

The thinnest BSCCO film that was studied was composed of ten layers of 2212 grown on top of two layers of carrier depleted 2201 and capped with one layer of carrier depleted 2201. The onset of the inductive transition is 85K and \( \lambda(4 \text{ K}) = 3300 \text{ Å} \). With a drive current of 300 \( \mu \text{A} \) at least six transitions are observed (Figure 34) ranging between 40 and 85 K. We believe that each transition is a layer or pair of layers going
Figure 34. Thin BSCCO film showing individual layers with different $T_c$ values. The inset is a graph of the phase of $M$. Each peak indicates a transition. The transitions are also visible in the $1/\lambda^2 (T)$ graph. The data were measured at three different drive currents, 300 $\mu$A, 15 $\mu$A, and 5 $\mu$A. The lowest drive current data show the superconducting 2201 layers.
superconducting. As the drive current is lowered a transition develops around 20K. For drive currents below 4 μA the data for this additional transition becomes independent of drive current. At 4 K the additional $1/\lambda^2$ (4 K) is about 2 μm$^2$ which corresponds to the number of carriers expected in a 2201 layer.

Three thicker BSCCO 2212 films were studied. The thicknesses of films B1248, B1337, and B1336 are 770 Å, 854 Å, and 1032 Å. Their low temperature penetration depths are 2700 Å, 2400 Å, and 3200 Å and their transition temperatures are 85 K, 83 K and 75 K respectively. The temperature dependence of $1/\lambda^2$ for the three films is the same except near the transition where film B1336 shows a steep drop (Figures 35,36).

At low temperatures $1/\lambda^2(T) - 1/\lambda^2(0) \sim T^2$ for all three of the films (Figure 37). Both $1/\lambda^2 (T) - 1/\lambda^2(0) \sim T$ and $1/\lambda^2(T) - 1/\lambda^2(0) \sim T^2$ has been observed in a single crystals of BSCO.$^{5,45,6}$ Crystals typically have a higher $T_C$ and a slightly lower penetration depth. If the lowered $T_C$ of the films is a result of disorder than the quadratic temperature dependence is a natural result of a slightly disordered d-wave order parameter.
Figure 35. $1/\lambda^2(T)$ for BSCCO 2212. In order of decreasing superfluid density the films are B1337, B1248, B1325, and B1336.
Figure 36. $\lambda^2(0)/\lambda^2(T)$ vs. $T/T_C$ BSCCO 2212. Data from the same four films of Figure 35 are shown.
Figure 37. Low temperature $\lambda$ for BSCCO 2212. The data were fit from 5 K to 30 K with a best fit quadratic of $\lambda(T) = 2378 \text{ Å} +0.13 \text{ Å/K}^2 T^2$
APPENDIX D

FREQUENCY DEPENDENCE OF THE COMPLEX CONDUCTIVITY

We have measured the frequency dependence of the complex conductivity of pure YBCO films at the superconducting to normal state transition. We find that for frequencies from 100 Hz to 100 kHz the peak in the real conductivity is proportional to $1/v$.

We determine the complex conductivity from the two coil experiment. The magnitude of the real part of the conductivity determined from the mutual inductance is very sensitive to the measured phase of the mutual inductance. It is important to accurately determine and remove the background effects of the probe when studying the real part of the conductivity. The background effects become negligible for frequencies under 20 kHz. Since the measurement is inductive the measured voltage is proportional to the frequency and the measurement is noisier for low frequencies.

Figure 38 shows the complex conductivity of a pure YBCO film measured at 50 kHz. For temperatures lower than the peak temperature the error in the real part of the conductivity grows and it is not possible to determine the temperature where $\sigma_1$ becomes zero. In the normal state at 100 K the real part of the conductivity is about 0.01 $(\mu\Omega\text{cm})^{-1}$.
Figure 38. Complex conductivity of a pure YBCO film (film 1).
We expect the imaginary part of the conductivity to vary as $1/\omega$ for these frequencies since $\sigma_\text{im} = 1/\mu_0 \omega \lambda^2$ and $\lambda$ should be independent of frequency. This is what is observed. However, we do not understand the behavior of the real part of the conductivity. The magnitude of real part of the conductivity is on the order of the magnitude of the imaginary part of the conductivity and the real part also varies strongly with frequency (Figure 39). Figure 40 shows the real part of the conductivity for frequencies from 1 kHz to 100 kHz. The same behavior has been measured in several pure YBCO films.

The peak in the real conductivity varies as $1/\omega$ in all of the samples that we have measured down to the lowest frequency accessible to us, 100 Hz (Figure 41). We find it very surprising that this frequency dependence persists to so low a frequency. If both parts of the complex conductivity vary as $1/\omega$ over enough decades then according to the Kramers-Kronig relations we would expect that the phase of the conductivity to be near $90^\circ$. The phase angle of our complex conductivity is near $45^\circ$, so our data appear to be in violation of the Kramers-Kronig relations. This is only possible if the data are a result of an inhomogeneous effect or vortex motion instead of an intrinsic bulk property.

We have found that both the real and imaginary part of the conductivity varies as $1/\omega$ for frequencies between 100 Hz and 100 kHz. We currently do not have an explanation for this behavior, but one possible explanation is that the frequency dependence is due to inhomogeneous Josephson junction type grain boundaries.
Figure 39. Complex conductivity of a pure YBCO film measured at 5 kHz and 50 kHz (film2).
Figure 40. The real part of the conductivity of a pure YBCO film measured at 1 kHz, 5 kHz, 10 kHz, 50 kHz, and 100 kHz. The peak of the data decreases with increasing frequency (film 2).
Figure 41. The peak of the real conductivity vs. frequency. $\sigma_1 \sim 1/\omega$ over 4 decades in frequency (film3). The slope of the straight line is 1 indicating $1/\omega$ behavior. The same result was found in other films.
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