CONVENTIONAL AND TIME-RESOLVED SPECTROSCOPY OF MAGNETIC PROPERTIES OF SUPERCONDUCTING THIN FILMS

By

XIAOXIANG XI

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2011
To my parents, Huahong Xi and Liping Zhu
ACKNOWLEDGMENTS

I owe my deepest gratitude to my advisor Dr. David B. Tanner, who provided me this exciting research opportunity and supported me throughout my graduate career. His knowledge, advice, and encouragement have always been invaluable to me. I am deeply indebted to Dr. G. Lawrence Carr at the Brookhaven National Laboratory. It has been a great honor to work with him, and to learn from him many experimental skills and intuitive understandings of physics. I would like to thank Dr. Christopher J. Stanton, Dr. David H. Reitze, Dr. Peter J. Hirschfeld, Dr. Arthur F. Hebard, and Dr. David P. Norton for serving on my supervisory committee and for their insightful comments. Acknowledgements also go to Dr. Mark W. Meisel for stimulating discussions.

It is a great pleasure to thank those who helped me making these experiments possible. In particular, I am grateful to Dr. Jungseek Hwang for enlightening me at the initial stage of this work. I would like to express my appreciation to Dr. Catalin Martin for carrying out some of the experiments together. The samples were provided by P. Bosland and E. Jacques at CEA Saclay. The four-probe resistivity measurements on these samples were done with the help of Dr. Ju-Hyun Park, Dr. David E. Graf, Mr. Timothy P. Murphy, and Dr. Stanley W. Tozer at the National High Magnetic Field Laboratory. Dr. Ricardo Lobo provided valuable data acquisition programs for the time-resolved experiment. I would also like to thank my colleagues in Tanner Lab from whom I learned a lot. Among them are Daniel Arenas, Richard Ottens, Dimitrios Koukis, Zahra Nasrollahi, Kevin Miller, and Naween Anand.

This project could not have progressed so smoothly without the help of many supporting staff. The user support group at the National Synchrotron Light Source, Gary Nintzel and Randy Smith in particular, provided technical support during all my visits. I would like to express my gratitude to the machine shop members of the UF Physics Department, who made several sample holders which were essential in my experiments. I
am also grateful to the electronic shop technicians for their help, and to the secretary staff for managing my trips to Brookhaven.

Finally, I would like to express my sincerest thanks to my family and my friends. My parents have always been steadfast believers in me. It was only with their constant love and continuous support that I could have completed this work.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>4</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>9</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>10</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>13</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>14</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1  INTRODUCTION</td>
<td>15</td>
</tr>
<tr>
<td>2  FUNDAMENTALS OF SUPERCONDUCTIVITY</td>
<td>18</td>
</tr>
<tr>
<td>2.1 History of Superconductivity</td>
<td>18</td>
</tr>
<tr>
<td>2.2 London Equations</td>
<td>19</td>
</tr>
<tr>
<td>2.3 BCS Theory</td>
<td>20</td>
</tr>
<tr>
<td>2.3.1 Microscopic Origin of Superconductivity</td>
<td>20</td>
</tr>
<tr>
<td>2.3.2 Energy Gap</td>
<td>21</td>
</tr>
<tr>
<td>2.3.3 Critical Temperature</td>
<td>22</td>
</tr>
<tr>
<td>2.3.4 Excitation Spectrum</td>
<td>22</td>
</tr>
<tr>
<td>2.3.5 Penetration Depth and Coherence Length</td>
<td>23</td>
</tr>
<tr>
<td>2.3.6 Optical Conductivity</td>
<td>24</td>
</tr>
<tr>
<td>2.4 Ginzburg-Landau Theory</td>
<td>26</td>
</tr>
<tr>
<td>2.4.1 Ginzburg-Landau Equations</td>
<td>27</td>
</tr>
<tr>
<td>2.4.2 Effective Penetration Depth</td>
<td>28</td>
</tr>
<tr>
<td>2.4.3 Ginzburg-Landau Coherence Length</td>
<td>28</td>
</tr>
<tr>
<td>2.4.4 Type I and Type II Superconductors</td>
<td>29</td>
</tr>
<tr>
<td>2.4.5 Vortex State</td>
<td>30</td>
</tr>
<tr>
<td>2.4.6 Thin-Film Superconductors</td>
<td>32</td>
</tr>
<tr>
<td>2.4.6.1 Critical current</td>
<td>32</td>
</tr>
<tr>
<td>2.4.6.2 Parallel critical field</td>
<td>33</td>
</tr>
<tr>
<td>2.4.6.3 Field distribution in parallel magnetic field</td>
<td>34</td>
</tr>
<tr>
<td>3  EXPERIMENT TECHNIQUES AND SAMPLES</td>
<td>35</td>
</tr>
<tr>
<td>3.1 Fourier Transform Infrared Spectroscopy</td>
<td>35</td>
</tr>
<tr>
<td>3.1.1 Principles</td>
<td>35</td>
</tr>
<tr>
<td>3.1.2 Sources in FT-IR</td>
<td>39</td>
</tr>
<tr>
<td>3.1.3 Detectors in FT-IR</td>
<td>40</td>
</tr>
<tr>
<td>3.2 Time-Resolved Infrared Spectroscopy</td>
<td>42</td>
</tr>
<tr>
<td>3.2.1 Principles</td>
<td>42</td>
</tr>
<tr>
<td>3.2.2 Laser-Pump Synchrotron-Probe Spectroscopy at NSLS</td>
<td>42</td>
</tr>
</tbody>
</table>
6 TIME-RESOLVED MAGNETO-SPECTROSCOPY OF CHARGE DYNAMICS

6.1 Introduction to Non-Equilibrium Superconductivity

6.2 Motivation

6.3 Experimental

6.4 Temperature Dependence

6.5 Field Dependence: Field Parallel to Sample Surface

6.5.1 Exponential-Decay Fit

6.5.2 Universal Scaling Behavior

6.5.3 Recombination Model

6.5.3.1 Recombination rate coefficient

6.5.3.2 Spin-polarization factor

6.5.3.3 Constant of proportionality

6.5.3.4 Total effect of magnetic fields

6.6 Field Dependence: Field Perpendicular to Sample Surface

6.7 Summary

7 CONCLUSIONS
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>Sample parameters</td>
<td>53</td>
</tr>
<tr>
<td>4-1</td>
<td>Pair-breaking parameter, effective spectroscopic gap, and pair-correlation gap</td>
<td>73</td>
</tr>
<tr>
<td>4-2</td>
<td>Superfluid density in parallel fields</td>
<td>78</td>
</tr>
<tr>
<td>5-1</td>
<td>Normal-volume fraction ( f )</td>
<td>110</td>
</tr>
<tr>
<td>5-2</td>
<td>Superfluid density in perpendicular fields</td>
<td>111</td>
</tr>
<tr>
<td>6-1</td>
<td>Fitting parameters for the temperature-dependent decay data of NbTiN</td>
<td>121</td>
</tr>
<tr>
<td>6-2</td>
<td>Fitting parameters for the NbTiN decay data in parallel fields at various fluences</td>
<td>129</td>
</tr>
<tr>
<td>6-3</td>
<td>Fitting parameters for the NbN decay data in parallel fields at various fluences</td>
<td>130</td>
</tr>
<tr>
<td>A-1</td>
<td>Conversion table for CGS and SI units</td>
<td>153</td>
</tr>
<tr>
<td>B-1</td>
<td>Relations between optical constants</td>
<td>156</td>
</tr>
</tbody>
</table>
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>BCS gap and density of states</td>
<td>22</td>
</tr>
<tr>
<td>2-2</td>
<td>Optical conductivity from BCS Mattis-Bardeen theory</td>
<td>25</td>
</tr>
<tr>
<td>3-1</td>
<td>Interferometer used in FT-IR</td>
<td>36</td>
</tr>
<tr>
<td>3-2</td>
<td>Laser focusing optics</td>
<td>44</td>
</tr>
<tr>
<td>3-3</td>
<td>Experimental set-up for time-resolved pump-probe spectroscopy at NSLS</td>
<td>47</td>
</tr>
<tr>
<td>3-4</td>
<td>Timing scheme for time-resolved pump-probe spectroscopy at NSLS</td>
<td>48</td>
</tr>
<tr>
<td>3-5</td>
<td>Resistance vs temperature</td>
<td>53</td>
</tr>
<tr>
<td>3-6</td>
<td>Transmittance of NbTiN and NbN at 20 K</td>
<td>55</td>
</tr>
<tr>
<td>3-7</td>
<td>Parallel upper critical fields $H^\parallel_{c2}$</td>
<td>57</td>
</tr>
<tr>
<td>3-8</td>
<td>Perpendicular upper critical fields $H^\perp_{c2}$</td>
<td>58</td>
</tr>
<tr>
<td>4-1</td>
<td>Sample holders for measurements in parallel magnetic fields</td>
<td>62</td>
</tr>
<tr>
<td>4-2</td>
<td>$\mathcal{T}_s/\mathcal{T}_n$ and $\mathcal{R}_s/\mathcal{R}_n$ in parallel fields</td>
<td>65</td>
</tr>
<tr>
<td>4-3</td>
<td>Comparison of $\mathcal{T}<em>s/\mathcal{T}<em>n$, $\mathcal{T}</em>{ext,s}/\mathcal{T}</em>{ext,n}$, $\mathcal{R}<em>s/\mathcal{R}<em>n$, and $\mathcal{R}</em>{ext,s}/\mathcal{R}</em>{ext,n}$</td>
<td>67</td>
</tr>
<tr>
<td>4-4</td>
<td>Zero-field optical conductivity obtained in parallel-field configuration</td>
<td>68</td>
</tr>
<tr>
<td>4-5</td>
<td>Optical conductivity of NbTiN in parallel fields</td>
<td>69</td>
</tr>
<tr>
<td>4-6</td>
<td>Optical conductivity of NbN in parallel fields</td>
<td>70</td>
</tr>
<tr>
<td>4-7</td>
<td>$\sigma_1/\sigma_n$ from Skalski’s theory</td>
<td>72</td>
</tr>
<tr>
<td>4-8</td>
<td>Field dependence of the pair-breaking parameter</td>
<td>74</td>
</tr>
<tr>
<td>4-9</td>
<td>Field dependence of the gaps</td>
<td>76</td>
</tr>
<tr>
<td>4-10</td>
<td>$\sigma_2/\sigma_n$ vs $1/\omega$ in parallel fields</td>
<td>79</td>
</tr>
<tr>
<td>4-11</td>
<td>Missing spectral weight in parallel fields</td>
<td>80</td>
</tr>
<tr>
<td>4-12</td>
<td>Comparison with Homes’s law</td>
<td>81</td>
</tr>
<tr>
<td>4-13</td>
<td>$\Delta(\Gamma), T_c(\Gamma)$, and $\Omega_G(\Gamma)$</td>
<td>82</td>
</tr>
<tr>
<td>4-14</td>
<td>Field dependence of the density of states</td>
<td>83</td>
</tr>
<tr>
<td>4-15</td>
<td>$\mathcal{T}_s/\mathcal{T}_n$ of NbTiN in parallel fields</td>
<td>86</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

$\lambda$ Penetration depth
$\xi$ Coherence length
$\Delta_0$ Single-particle gap at zero temperature and zero magnetic field
$\sigma$ Optical conductivity
$\mathcal{T}$ Transmittance
$R$ Reflectance

**Subscript** $s$ Used to denote the superconducting state

**Subscript** $n$ Used to denote the normal state

$R_{\square}$ Sheet resistance

$\Phi_0$ Magnetic flux quantum (approximately $2.068 \times 10^{-15}$ Wb)

$Z_0$ Impedance of free space (approximately 376.730 Ω)

$\Delta$ Pair-correlation gap (order parameter)

$2\Omega_G$ Effective spectroscopic gap

$\Gamma$ Pair-breaking parameter

$n_s$ Superfluid density

$f$ Normal volume filling fraction

$N$ Total quasiparticle density

$N_{th}$ Thermal quasiparticle density

$N_{ex}$ Excess quasiparticle density

$S$ Photo-induced transmission signal (integrated signal)

$dS/dt$ Differential signal

$R$ Recombination rate coefficient

$\tau_R$ Intrinsic quasiparticle lifetime

$\tau_B$ Phonon pair-breaking lifetime (lifetime of phonons giving rise to the bottleneck effect)

$\tau_\gamma$ Phonon escaping time (lifetime of phonons escaping the sample without pair breaking)

$\mathcal{F}$ Laser fluence
CONVENTIONAL AND TIME-RESOLVED SPECTROSCOPY OF MAGNETIC PROPERTIES OF SUPERCONDUCTING THIN FILMS

By

Xiaoxiang Xi

December 2011

Chair: David B. Tanner
Major: Physics

The magnetic properties of two thin-film type-II superconductors are investigated by optical spectroscopy. We first performed conventional Fourier-transform infrared spectroscopy on the Nb$_{0.5}$Ti$_{0.5}$N and NbN samples in a magnetic field. When the field is parallel to the film surface, it breaks the time-reversal symmetry of the Cooper pairs in the thin sample and causes spatial variation of the order parameter in the thick sample, both resulting in pair-breaking effects. The extracted optical conductivity is consistent with the pair-breaking theory. When the field is perpendicular to the film surface, it creates vortices in both samples and weakens the strength of superconductivity. The optical conductivity data of the two samples are consistent with the Maxwell-Garnett theory. We also demonstrated that the pair-breaking effects should be included for an accurate description of the effective electrodynamic response in the mixed state. After elucidating these magnetic-field-dependent equilibrium state properties, we performed time-resolved infrared spectroscopy to study the charge dynamics in these superconducting thin films after photo-excitation. We found that the quasiparticle recombination process is significantly slowed by a parallel magnetic field. The effective recombination rate scales linearly with the photo-induced excess quasiparticle signal, with the slope showing strong field dependence. Our recombination model explains the field dependence through the field-induced pair breaking.
In a conventional superconductor, superconductivity originates from the pair correlation of electrons through electron-phonon interaction, a well-known mechanism from the Bardeen-Cooper-Shriffer (BCS) theory [1, 2]. Each pair consists of electrons of opposite momentum and spin ($\mathbf{k} \uparrow, -\mathbf{k} \downarrow$), therefore having time-reversal symmetry. Conventional superconductors are categorized into two types according to their response to a magnetic field [3]. A type I superconductor exhibits perfect diamagnetism up to a critical magnetic field $H_c$, above which superconductivity is destroyed. A type II superconductor shows perfect diamagnetism below a lower critical field $H_{c1}$, and reverts to the normal state above an upper critical field $H_{c2}$. In the intermediate regime where $H_{c1} < H < H_{c2}$, the magnetic field partially penetrates the superconductor in the form of quantized flux lines (vortices). Superconductivity is quenched in the core region of vortices, around which supercurrents persist. Outside of the vortices, superconductivity is maintained. The whole system is therefore in a mixed state in this intermediate regime.

More generally a magnetic field perturbs the superconducting state by coupling to the electron orbital motion or by aligning the electron spin, leading to pair breaking and weakening of superconductivity [4, 5]. When the field is strong enough, the effect on the electron orbital motion results in the destruction of superconductivity and determines the critical fields mentioned above. Recent studies also found a surprising opposite limit where magnetic fields can be used to enhance superconductivity [6–10]. The magnetic response of a superconductor is therefore revealing because it points to the mechanism behind this fascinating phenomenon. Knowledge of the magnetic properties is also essential to material applications, because superconducting devices typically carry electric current which inevitably generates a magnetic field.

Infrared spectroscopy is a powerful tool to investigate condensed-matter systems. Through interactions with electromagnetic waves, excitations in materials can be
sensitively probed. Such experiments typically yield the optical constants of materials through model-independent analysis, which can be used as a stringent test to existing models and theories for the materials under study [11]. Far-infrared spectroscopy is particularly useful for studying superconductivity. Because the typical energy scale of superconducting energy gaps falls in the far-infrared range, this technique is capable of capturing this signature of superconductivity [11, 12]. It is also highly sensitive to condensation formation or loss, because the excitations relevant to the formation of the superconducting state exist in the far-infrared. Combined with variable experiment conditions such as temperature and magnetic field, it provides valuable insight to the pairing mechanism. Such advantages are empowered by using synchrotron radiation as the source of spectroscopy. At the National Synchrotron Light Source, Brookhaven National Laboratory, we have access to a magneto-optical set-up that delivers infrared light orders-of-magnitude brighter than conventional sources and reaches the lower end of the far-infrared spectral range. Moreover, the pulsed feature of synchrotron radiation combined with a fast infrared laser is ideal for studying non-equilibrium processes in superconductors.

In this dissertation, we present spectroscopic studies of magnetic properties of type-II superconductors. The samples are Nb0.5Ti0.5N (abbreviated as NbTiN hereafter) and NbN thin films on dielectric substrates, suitable for transmission and reflection measurements. Thin-film samples are also interesting because of the anisotropy due to the sample geometry. On the one hand, when a magnetic field is applied normal to the film surface, vortices are created. Thin film samples in this case are therefore essentially equivalent to bulk samples. The electrodynamics response of superconductors in the vortex state is investigated to test various theories describing this phase of matter. On the other hand, when a magnetic field is applied parallel to the film surface, one may minimize or even avoid vortex-induced effects, so that any other interactions between the magnetic field and the superconducting electrons can be studied. Tunneling technique was applied for this
kind of study in the past [13, 14], but optical studies are rare. Our goal is to establish a reliable magneto-optical technique that tackles these problems from a new perspective.

This work is also motivated by understanding the quasiparticle dynamics in a superconductor under the influence of a magnetic field. The field was thought to create vortices as extra channels for quasiparticle relaxation, expediting the relaxation process. Our experiment found unexpected slowing of the relaxation. We first determine how magnetic fields affect the equilibrium superconducting state. Such information assists our understanding of the non-equilibrium state.

This dissertation is organized in the following fashion. It begins with an introduction to the fundamentals of conventional superconductivity in Chapter 2. Many concepts and well-developed facts are summarized to be applied in later chapters. Chapter 3 explains the experimental techniques and characterizes the samples by determining the material parameters. In Chapter 4 and Chapter 5 we employ Fourier transform infrared spectroscopy to extract the optical conductivity of two thin-film samples in both parallel and perpendicular magnetic fields. The data are interpreted in terms of the pair-breaking effects in the former case, and the effective electrodynamic response of the vortex state in the latter. In Chapter 6 we probe the quasiparticle recombination dynamics using time-resolved pump-probe spectroscopy. The non-equilibrium results are analyzed based on the equilibrium-state properties studied in Chapter 4 and Chapter 5. Chapter 7 summarizes the main results and points out topics for future studies.

In infrared spectroscopy it is conventional to use wavenumbers as the unit of frequency. The wavenumber is defined as the reciprocal of the wavelength or the number of wavelength per unit distance, with the unit cm$^{-1}$. 1 cm$^{-1}$ corresponds to a wavelength of 1 cm and a frequency of 30 GHz. In the field of superconductivity CGS units are preferred. These conventions are followed throughout this dissertation. Conversions from CGS units to SI units are included in Appendix A for reference.
2.1 History of Superconductivity

One century ago, soon after he established the techniques of liquefying helium, H. Kamerlingh Onnes discovered superconductivity in mercury [15]. The mystery of this phenomenon has attracted great attention of scientists ever since then. Two decades later, Walther Meissner and Robert Ochsenfeld found that superconductors repel magnetic fields [16]; the perfect diamagnetism is referred to as the Meissner effect. Subsequently, superconductivity was discovered in a variety of metals, alloys, and compounds, some with the critical temperature ($T_c$) above 10 K, e.g. Ref. [17]. Meanwhile theoretical understanding of the mechanism of superconductivity was under progress. In 1935, F. and H. London proposed two equations to describe the electrodynamical properties of superconductors [18], which explained the Meissner effect. In 1950 Ginzburg and Landau proposed a phenomenological theory that successfully described the macroscopic properties of superconducting electrons [19]. A true breakthrough was the theory by Bardeen, Cooper, and Schriffer in 1957 [1, 2], which for the first time explained the microscopic origin of superconductivity as the condensation of electron pairs mediated by electron-phonon interaction. The field was revitalized in 1986 when IBM researchers Bednorz and Müller synthesized a ceramic compound composed of lanthanum, barium, cooper, and oxygen, which surprisingly superconducts at 30 K [20]. One year later when researchers substituted yttrium for lanthanum, a superconductor with $T_c$ of 92 K was discovered [21], being the first material that superconducts at a temperature greater than liquid nitrogen. This significantly reduces the cost of cooling, making high-temperature superconductors popular candidates for various applications [22, 23]. The term high-temperature superconductors was commonly used interchangeably with cuprates, which stands for cooper-oxide superconductors, until a few years ago a new family of superconductors was found in layered iron arsenide materials with $T_c$ as high
as 56 K [24, 25]. The various families of high-temperature superconductors share some common features but are also dramatically different in many aspects [26]. Up to now there is no unified theory on the mechanism of high-temperature superconductors.

In this dissertation we will deal with conventional metallic s-wave superconductors. Therefore some of their basic properties related to our studies will be reviewed in this chapter. Since the theories of conventional superconductors are relatively complete, the following review is theory-based, citing important conclusions for the use in later chapters. More details of this subject can be found in Refs. [3, 27–31].

2.2 London Equations

The London equations are two equations relating the current and electromagnetic waves in a superconductor. F. and H. London adopted the two fluid model of C. J. Gorter and H. B. G. Casimir [32], in which it was proposed that the total density of electrons is comprised of two components, one of which is condensed into “superfluid” that is responsible for the superconducting properties, and the other form an inter-penetrating fluid of “normal” electrons. The superconducting electrons are treated as an ideal electron gas with density $n_s$, which is limited by the total density of conduction electrons $n$ in the system and has the empirical temperature dependence

$$n_s(t) = n \left[ 1 - \left( \frac{T}{T_c} \right)^4 \right]. \quad (2-1)$$

The London brothers argued that an external electric field $E$ could freely accelerate the superconducting electrons, making them flow without resistance and creating a supercurrent of current density $J_s$. The first London equation describes this phenomenon of perfect conductivity,

$$\frac{\partial J_s}{\partial t} = \frac{n_s e^2}{m} E. \quad (2-2)$$

This equation is reminiscent of Ohm’s law, $J = \sigma E = (n e^2 \tau/m) E$, where $n$ is the free electron number density and $\tau$ is the electronic mean free time between ionic collisions.
It is evident from this equation that to use the London equations, the response of the superconducting electrons to the external fields should be local.

The second London equation,

$$\nabla \times J_s = -\frac{n_s e^2}{mc} H,$$

(2-3)

together with $$\nabla \times H = (4\pi/c) J_s$$ from Maxwell’s equations, yields

$$\nabla^2 H = \frac{H}{\lambda_L^2}.$$

(2-4)

\(H\) represents the local value of the magnetic field, which varies over the length scale

$$\lambda_L = \sqrt{\frac{mc^2}{4\pi n_s e^2}},$$

(2-5)
called the London penetration depth, typically tens of nanometers in metallic superconductors [28]. Eq. (2-4) therefore explain the Meissner effect: the external magnetic field is shielded from the interior of bulk superconductors. Since \(n_s \leq n\), \(\lambda_L\) has the minimum value at 0 K, \(\lambda_L(0) = \sqrt{mc^2/4\pi n e^2}\), and diverges at \(T_c\) according to the temperature dependence of \(n_s\) given by Eq. (2-1),

$$\lambda_L(T) = \frac{\lambda_L(0)}{\sqrt{1 - (T/T_c)^4}}.$$

(2-6)

2.3 BCS Theory

2.3.1 Microscopic Origin of Superconductivity

The BCS theory successfully explains the microscopic mechanism of superconductivity. Superconductivity arises because electrons form pairs and condense in the ground state. The theory does not rely on the specific mechanism of pairing, as long as the attractive interaction exists. In reality, the pairing between electrons is mediated by phonons: one electron polarizes the surrounding medium by attracting positive ions from the lattice, which in turn attracts a second electron. The effective attraction between these two electrons overrides their Coulomb repulsion, and a Cooper pair is formed.
Superconductivity can only occur at sufficiently low temperatures when electrons near the Fermi surface become unstable against the formation of Cooper pairs. Quantitative results of the BCS theory are in the weak coupling limit when the attractive interaction between paired electrons is small.

### 2.3.2 Energy Gap

BCS theory finds an energy gap between the ground state and the quasiparticle excitation state. The existence of a gap in the superconducting state was hinted by the \( e^{-a/k_BT} \) (\( a > 0 \)) temperature dependence of the electronic specific heat at low temperature, and confirmed by electromagnetic absorption spectrum. In the ground state at 0 K, the gap \( \Delta_0 \) is obtained from

\[
\frac{1}{N(0)V} = \int_0^{\hbar\omega_c} \frac{d\xi}{\sqrt{\xi^2 + \Delta_0^2}} = \sinh^{-1}\frac{\hbar\omega_c}{\Delta_0},
\]

where \( N(0) \) is the density of states at the Fermi energy for electrons of one spin orientation, \( V \) is the paring potential, and \( \hbar\omega_c \) is the cut-off energy characterizing the potential \( V \) above which the pairing potential is zero. \( \hbar\omega_c \) is of the order of the Debye energy \( \hbar\omega_D \) that characterizes the cut-off of the phonon spectrum. In metals it is typically tens of meV. In the weak coupling limit \( N(0)V \ll 1 \),

\[
\Delta_0 \approx 2\hbar\omega_c e^{-1/N(0)V}.
\]

This result indicates that \( \Delta_0 \) is only a very small fraction of the Debye energy.

The temperature dependence of the gap \( \Delta(T) \) is obtained from the integral

\[
\frac{1}{N(0)V} = \int_0^{\hbar\omega_c} \frac{\tanh \left( \sqrt{\xi^2 + \Delta^2}/2k_BT \right)}{\sqrt{\xi^2 + \Delta^2}} d\xi.
\]

\( \Delta(T) \) is solved numerically and plotted in the left panel of Figure 2-1. It can be well approximated by the analytical form

\[
\frac{\Delta}{\Delta_0} = \sqrt{\cos \left[ \frac{\pi}{2} \left( \frac{T}{T_c} \right)^2 \right]}.
\]
Figure 2-1. Left: temperature dependence of the BCS gap. Right: BCS density of states.

$\Delta$ remains very close to $\Delta_0$ at sufficiently low temperatures when $T/T_c \ll 1$. It drops monotonically as the temperature increases, and drastically approaches zero at the transition temperature $T_c$. Note that as $T \to T_c$, $\Delta(T) \propto \sqrt{1 - (T/T_c)^2}$ according to the approximation given by Eq. (2–10), while the exact form from Eq. (2–9) yields $\Delta(T) \propto \sqrt{1 - T/T_c}$.

### 2.3.3 Critical Temperature

The critical (or transition) temperature $T_c$ can be determined from Eq. (2–9) by setting $\Delta$ to zero. It yields

$$k_B T_c \approx 1.13 \hbar \omega_c e^{-1/N(0)V}.$$  \hspace{1cm} (2–11)

From this and Eq. (2–8) we see that in the weak coupling limit,

$$\frac{\Delta_0}{k_B T_c} \approx 1.76,$$  \hspace{1cm} (2–12)

in good agreement with experimental values.

### 2.3.4 Excitation Spectrum

The existence of electron pairs and the gap $\Delta$ requires that generations of excited quasiparticles are also created in pairs, consuming energy of $2\Delta$ (termed the spectroscopic gap). The term quasiparticle is to distinguish it from normal free electrons, because in
superconductors there are interactions between these excited electrons and the rest of the system. These quasiparticles have energy $E_k = \sqrt{\xi_k^2 + |\Delta_k|^2}$, where $\xi_k$ is the single-particle energy relative to the Fermi energy, and $\Delta_k$ plays the role of an energy gap. The thermal distribution of quasiparticles obeys the Fermi-Dirac function

$$f(E_k) = \frac{1}{e^{E_k/k_B T} + 1},$$  \hspace{1cm} (2–13)

with $E_k$ is equal to or greater than the single-particle gap $\Delta$.

The single-particle density of states $N_s(E)$ is given as

$$\frac{N_s(E)}{N(0)} = \begin{cases} \frac{E}{\sqrt{E^2 - \Delta^2}} & (E > \Delta) \\ 0 & (E < \Delta) \end{cases}$$  \hspace{1cm} (2–14)

shown in the right panel of Figure 2-1. The figure shows that quasiparticles only exist with energy greater than the single-particle gap $\Delta$. The density of states diverges at the gap, indicating that quasiparticles tend to accumulate just above the gap.

### 2.3.5 Penetration Depth and Coherence Length

It was mentioned before that the London penetration depth $\lambda_L$ is only valid in the local limit. The BCS theory gives a solution to the more general penetration depth $\lambda$ that can be applied to both the local and non-local limit. The non-local limit applies to materials with high Fermi velocity $v_F$, low $T_c$, and long mean free path $l$, and was discussed by Pippard [33] before the BCS theory. BCS theory finds $\lambda \approx (\lambda_L^2 \xi_0)^{1/3}$ in this limit, where $\xi_0$ is the BCS coherence length

$$\xi_0 \equiv \frac{\hbar v_F}{\pi \Delta_0}.$$  \hspace{1cm} (2–15)

$\xi_0$ is a measure of the distance between the two electrons in a Cooper pair.

Both the penetration depth and the coherence length depend on the purity of the superconducting materials. For type-II superconductors (defined below in Section 2.4.4) in
the dirty limit,\(^1\) with electron mean free path \(l\), the penetration depth and the coherence length are \([28]\)

\[
\lambda \approx \lambda_L \left( \frac{\xi_0}{L} \right)^{1/2},
\]

\(\xi \approx (\xi_0)^{1/2}.\)

2.3.6 Optical Conductivity

Mattis and Bardeen derived the optical conductivity of a BCS superconductor in the dirty limit, well known as the Mattis-Bardeen theory \([34]\). Define the complex optical conductivity as \(\sigma = \sigma_1 + i\sigma_2\). According to this theory, the real and imaginary parts of the optical conductivity of dirty-limit superconductors are

\[
\frac{\sigma_1}{\sigma_n}(\omega) = \frac{2}{\hbar \omega} \int_{\Delta}^{\infty} \left[ f(E) - f(E + \hbar \omega) \right] \frac{E}{\sqrt{E^2 - \Delta^2}} \frac{E + \hbar \omega}{\sqrt{(E + \hbar \omega)^2 - \Delta^2}} \left[ 1 + \frac{\Delta^2}{E(E + \hbar \omega)} \right] dE
\]

\[
+ \frac{1}{\hbar \omega} \int_{\Delta - \hbar \omega}^{-\Delta} \left[ 1 - 2f(E + \hbar \omega) \right] \left| \frac{E}{\sqrt{E^2 - \Delta^2}} \frac{E + \hbar \omega}{\sqrt{(E + \hbar \omega)^2 - \Delta^2}} \right| \left[ 1 + \frac{\Delta^2}{E(E + \hbar \omega)} \right] dE,
\]

\(\frac{\sigma_2}{\sigma_n}(\omega) = \frac{1}{\hbar \omega} \int_{\Delta - \hbar \omega}^{\Delta} \left[ 1 - 2f(E + \hbar \omega) \right] \frac{E}{\sqrt{\Delta^2 - E^2}} \frac{E + \hbar \omega}{\sqrt{(E + \hbar \omega)^2 - \Delta^2}} \left[ 1 + \frac{\Delta^2}{E(E + \hbar \omega)} \right] dE.
\)

Here \(\sigma_n\) is the normal-state optical conductivity, \(\Delta\) is the temperature-dependent gap given by Eq. (2–9), and \(f(E)\) is the Fermi-Dirac function. The second integral in Eq. (2–18) does not appear unless \(\hbar \omega > 2\Delta\), in which case the lower limit in the integral of Eq. (2–19) should be \(-\Delta\). The second integral in Eq. (2–18) is therefore the contribution from photo-excited quasiparticles, and the first integral in Eq. (2–18) is the contribution from thermally-excited quasiparticles. Numerical results of Eqs. (2–18) and (2–19) at \(T = 0\) K are shown in Figure 2-2. The real part increases with a finite slope just above

\(^1\) The impurity concentration in a superconductor is characterized by the ratio \(l/\xi_0\). If \(l/\xi_0 \gg 1\), the material is said to be clean, while for \(l/\xi_0 \ll 1\), the material is dirty.
the optical gap $2\Delta_0$, even though at the single-particle gap the density of states diverges.

This is because the coherence factor of the form $1 + \Delta^2/E(E + \hbar\omega)$ in Eq. (2–18) increases gradually just above the single-particle gap. Such a factor arises because the superconducting state consists of phase-coherent superposition of states $(k \uparrow, -k \downarrow)$ occupied or unoccupied as a unit. When calculating the electromagnetic absorption as a scattering process, interference terms appear in the transition probability, which is absent in the normal state.

The oscillator-strength sum rule

$$\int_0^\infty \sigma_1(\omega)d\omega = \frac{\pi ne^2}{2m}, \quad (2–20)$$

requires that the area under $\sigma_1(\omega)$, defined as the spectral weight, should be conserved for both the normal and superconducting states. Here $n$ is the total electron density, and $e$ and $m$ are the charge and mass of the electron. The ratio $\sigma_1/\sigma_n$ in Figure 2-2 is always less than unity. The “missing area” (or the missing spectral weight) $A = \pi n_e e^2/2m$
condenses to a $\delta$ function at zero frequency, which is a measure of the condensate density [35]. The real part can therefore be written as

$$\sigma_1(\omega) = A\delta(0) + \sigma_{1,>}(\omega) = \frac{\pi n_s e^2}{2m} \delta(0) + \sigma_{1,>}(\omega), \quad (2-21)$$

where $\sigma_{1,>}(\omega)$ denotes the part of $\sigma_1$ at finite frequency plotted in the left panel of Figure 2-2. The imaginary part is related to the real part through the following Kramers-Kronig relation,

$$\sigma_2(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\sigma_1(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (2-22)$$

where $\mathcal{P}$ denotes the principal value of the integral. According to this equation, the imaginary part of the optical conductivity has the following form,

$$\sigma_2(\omega) = \frac{A}{\pi \omega} + \sigma_{2,>}(\omega) = \frac{n_s e^2}{2 m \omega} + \sigma_{2,>}(\omega), \quad (2-23)$$

where $\sigma_{2,>}(\omega)$ denotes the part of $\sigma_2$ related to $\sigma_{1,>}(\omega)$. The contribution from the two terms in $\sigma_2$ are compared in the right panel of Figure 2-2. Clearly, the term coming from the $\delta$ function in $\sigma_1$ dominates the behavior of $\sigma_2$ below the gap, and is responsible for the almost frequency independent penetration depth $\lambda = c/\sqrt{4\pi \omega \sigma_2}$. These properties of $\sigma_1$ and $\sigma_2$ are observed in most metallic superconductors (Sn, In, Pb, Hg, etc.), although strong-coupling effects are sometimes necessary for quantitative agreement [36–40].

The optical conductivity of BCS superconductors with arbitrary electron mean free path is discussed by W. Zimmermann et al. in Ref. [41].

2.4 Ginzburg-Landau Theory

Ginzburg and Landau introduced a complex order parameter $\psi(\mathbf{r})$ as the pseudo wavefunction of the superconducting electrons. $\psi(\mathbf{r})$ is proportional to the gap parameter $\Delta(\mathbf{r})$. $|\psi(\mathbf{r})|^2$ represents the local superfluid density $n_s^*(\mathbf{r})$. In the BCS theory, the gap is homogeneous. Ginzburg-Landau theory deals with a more general case in which spatial inhomogeneity exists, e.g. inhomogeneity induced by an external magnetic field, which
could be present in our field dependent studies. The gap can vary with position, and is generally complex. Gor’kov proved that the Ginzburg-Landau theory is a limiting case of the BCS theory [42].

### 2.4.1 Ginzburg-Landau Equations

The theory begins with the construction of the free energy of a superconductor. When \( \psi \) is small and varies slowly in space, the free energy density \( f \) has the form

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

where \( f_{n0} \) is the normal-state free energy density in the absence of magnetic fields, \( e^* = 2e \), \( m^* = 2m \), \( A \) is the vector potential corresponding to the microscopic magnetic field \( H \), and \( H^2/8\pi \) represents magnetic energy in vacuum. The coefficients \( \alpha \) and \( \beta \) are discussed below, given by Eqs. (2–34) and (2–35). Minimizing \( f \) with respect to fluctuations in the order parameter \( \psi \) and vector potential \( A \) yields the equation,

\[
\alpha \psi + \beta |\psi|^2 \psi + \frac{1}{2m^*} \left( \frac{\hbar}{i} \nabla - \frac{e^*}{c} A \right) \psi = 0,
\]

which determines the order parameter \( \psi = \psi(\alpha, \beta, A(r)) \). With this solution, the supercurrent density can be evaluated,

\[
J_s = \frac{e^* \hbar}{2m^*} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{e^* c^2}{m^* e} |\psi|^2 A.
\]

Eqs. (2–25) and (2–26) are the famous Ginzburg-Landau equations.

Because both equations specialize to a position \( r \), the Ginzburg-Landau theory is a local theory. Note that in the London gauge the London equations Eqs. (2–2) and (2–3) can be written as a single equation, \( J_s = -n_s e^2 A/mc \) [28]. Comparing this with Eq. (2–26), we see that the Ginzburg-Landau theory predicts an extra term in the supercurrent density which originates from the spatial variation of the order parameter. Eq. (2–26) therefore reduces to the form given by London equations in the limit that the order parameter is spatially homogeneous.
2.4.2 Effective Penetration Depth

According to Eq. (2–25), in the weak field limit, to the first order in \( H \), \( \psi^2 \) can be approximated as its zero-field value

\[
|\psi_\infty|^2 = -\frac{\alpha}{\beta},
\]

which is space independent. Taking the curl of Eq. (2–26) and using \( \nabla \times H = (4\pi/c)J_s \) yields,

\[
\nabla^2 H = \frac{4\pi e^2 |\psi|^2}{m^* c^2} H.
\]

Therefore the magnetic field is screened according to an effective penetration depth

\[
\lambda_{\text{eff}} = \sqrt{m^* c^2 \frac{4\pi e^2}{4\pi\alpha e^*}}.
\]

As the temperature approaches \( T_c \), \( |\psi|^2 \) is driven to 0, and \( \lambda_{\text{eff}} \) diverges. Noting that \( m^* = 2m, e^* = 2e \), and \( |\psi|^2 = n_s^* = n_s/2 \) as the Cooper pair density, \( \lambda_{\text{eff}} \) is consistent with the London penetration depth \( \lambda_L \) given as Eq. (2–5).

2.4.3 Ginzburg-Landau Coherence Length

In the absence of fields or currents, and for real \( \psi \) with the form \( \psi = \psi_\infty y \), Eq. (2–25) becomes

\[
\xi^2 \frac{d^2 y}{dx^2} + y - y^3 = 0,
\]

where \( \xi \) is the Ginzburg-Landau coherence length

\[
\xi = \frac{\hbar}{\sqrt{2m^* |\alpha|}}.
\]

From Eq. (2–30) it is clear that \( \xi \) is the characteristic length for the variation of \( y \) (or equivalently \( \psi \)). In other words, it gives an approximate spatial dimension of Cooper pairs.

The thermodynamic critical field \( H_c \) is defined from the superconducting-state free energy density \( f_s \) and the normal-state free energy density \( f_n \) as

\[
-\frac{H_c^2}{8\pi} = f_s - f_n = -\frac{\alpha^2}{2\beta},
\]
which has the empirical temperature dependence

\[ H_c(T) \approx H_c(0) \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]. \]  

(2–33)

Eqs. (2–32), (2–27), and (2–29) determine the coefficients \( \alpha \) and \( \beta \) in terms of the measured quantities \( \lambda_{\text{eff}} \) and \( H_c \),

\[ \alpha = -\frac{2e^2}{mc^2} H_c^2 \lambda_{\text{eff}}^2, \]  

(2–34)

\[ \beta = \frac{16\pi e^4}{m^2c^4} H_c^2 \lambda_{\text{eff}}^4. \]  

(2–35)

Substituting Eq. (2–34) into Eq. (2–31) yields

\[ \xi(T) = \frac{\Phi_0}{2 \sqrt{2} \pi H_c(T) \lambda_{\text{eff}}(T)}, \]  

(2–36)

in which \( \Phi_0 = \frac{hc}{2e} = 2.068 \times 10^{-15} \) Wb is the fluxoid quantum (or magnetic flux quantum). The Ginzburg-Landau coherence length \( \xi \) differs from the BCS coherence length \( \xi_0 \) given in Eq. (2–15), but the two are related. Using Eq. (2–15), \( H_c^2(0)/8\pi = \frac{1}{2} N(0) \Delta_0^2 \), and \( N(0) = 3n/4E_F \) for free electrons, one can derive that

\[ \frac{\xi(T)}{\xi_0} = \frac{\pi}{2 \sqrt{3}} \frac{H_c(0) \lambda_L(0)}{H_c(T) \lambda_{\text{eff}}(T)}. \]  

(2–37)

It turns out that at very low temperature the Ginzburg-Landau coherence length is approximately the same as the BCS coherence length.

**2.4.4 Type I and Type II Superconductors**

Type I superconductors are totally characterized by the Meissner effect, and have a critical field defined as the thermodynamic critical field \( H_c \) given by Eq. (2–32). Stronger perturbations induced by the field greater than \( H_c \) destroys superconductivity. Simple metallic superconductors such as pure samples of lead, mercury, and tin belong to this type. They usually have small penetration depth \( \lambda \) (for simplicity the subscript “eff” is omitted hereafter, and \( \lambda \) means the effective penetration depth \( \lambda_{\text{eff}} \) unless otherwise stated), but high Fermi velocity thus large coherence length, making \( \lambda < \xi \).
In the opposite limit when \( \lambda \) is much greater than \( \xi \), it would be energetically favorable for high magnetic fields to penetrate partially the superconductor and reduce the magnetic energy without reducing the condensation energy. At fields below the lower critical field \( H_{c1} \) the superconductor still exhibits the Meissner effect. Above \( H_{c1} \) and below the upper critical field \( H_{c2} \), fields partially penetrate the superconductor in the form of quantized flux tubes (vortices), each carrying a flux of \( \Phi_0 \) along the direction of the applied field. Theoretically these tubes form a regular array, but in practice symmetries of the underlying crystal structure or the defects in the materials determine the vortex distribution. The core region of a vortex is simplified as a cylinder with a radius of the coherence length \( \xi \), in which the superconducting state is quenched. The surrounding region of radius \( r < \lambda \) is the electromagnetic region where field and supercurrents persist. The whole material is therefore in a mixed state in this intermediate regime \( H_{c1} < H < H_{c2} \). Fields higher than \( H_{c2} \) drive the superconductor normal. Such superconductors are called type II superconductors. Examples include transition metals and alloys such as Nb\(_3\)Sn and NbTi. High-temperature superconductors can also be included in this category.

The ratio of \( \lambda \) and \( \xi \) is defined as the Ginzburg-Landau parameter \( \kappa \),

\[
\kappa = \frac{\lambda}{\xi},
\]

which distinguishes type I and type II superconductors, with \( \kappa = 1/\sqrt{2} \) as the crossover value. Superconductors with \( \kappa < 1/\sqrt{2} \) are called type I superconductors, while those with \( \kappa > 1/\sqrt{2} \) are type II superconductors.

### 2.4.5 Vortex State

Using the Ginzburg-Landau theory, Abrikosov predicted the existence of type-II superconductors and the mixed state when \( \kappa > 1/\sqrt{2} \), well before such phenomena were experimentally observed [43]. For type II superconductors the Ginzburg-Landau theory
finds $H_{c1}$ in the limit $\kappa \ll 1$ to be

$$H_{c1} = \frac{\ln \kappa}{\sqrt{2k}} H_c,$$  \hspace{1cm} (2–39)

and $H_{c2}$ in the general case to be

$$H_{c2} = \frac{\Phi_0}{2\pi \xi^2} = \frac{4\pi H_c^2 \lambda^2}{\Phi_0} = \sqrt{2k} H_c.$$  \hspace{1cm} (2–40)

In getting the last two equalities in Eq. (2–40), Eq. (2–36) and (2–38) are used. If $H_{c1} < H < H_{c2}$, the superconductor is in the mixed state in which vortices are present.

It is usually assumed that the vortex cores are normal and the material outside of the cores are fully superconducting; the transition occurs abruptly between these two regions at the core radius $\sim \xi$. Although the Ginzburg-Landau theory finds solutions to the vortex state with $\psi(r)$ non-zero except for $r$ exactly equal to zero, the above oversimplified model is rooted in experimental findings and have considerable validity.

If any transport current $J$ is present, there will be a Lorentz force exerted on the vortices, $f = J \times \Phi_0/c$, where the direction of $\Phi_0$ is parallel to the magnetic flux density. This force tends to move the vortices transverse to the current and induces changes in the magnetic flux. This in turn generates an electric field $E$, which causes dissipation proportional to $J \cdot E$. However, spatial inhomogeneities such as those caused by impurities could result in a pinning force which counteracts the Lorentz force. If sufficiently strong, such a pinning force can make vortex motion small enough so that dissipation is minimal and perfect conductivity retains. If this force is small, vortices will move at a steady rate; the material is in the flux flow regime characterized by a flux flow resistivity $\rho_f \approx \rho_n H/H_{c2}$ where $\rho_n$ is the normal-state resistivity.

In such a current-carrying superconductor, thermal energy at finite temperatures may lower the effective energy barrier of the pinning sites, activating flux lines to jump from one pinning center to another. Such kind of process, called flux creep, generates an observable voltage in the superconductor and causes dissipation.
2.4.6 Thin-Film Superconductors

Thin film superconductors differ from bulk superconductors in their magnetic properties. Consider a thin film superconductor of thickness \( d \) in the limit \( d \ll \xi \). Assume the spatial variation of the amplitude of the pseudo-wavefunction \( |\psi| \) can be neglected, so that \( \psi(\mathbf{r}) = |\psi|e^{i\phi(\mathbf{r})} \). The Ginzburg-Landau theory can be used to calculate the critical current and the parallel critical field of the thin film. The field distribution is also solved below.

2.4.6.1 Critical current

Let a supercurrent density \( J_s \) flow in the plane of the film. We also confine the discussion to the limit \( d \ll \lambda \) so that \( J_s \) can be assumed constant. The supercurrent density \( J_s \) from Eq. (2–26) in these limits is

\[
J_s = \frac{2e}{m^*} \left( \hbar \nabla \phi - \frac{2e}{c} A \right) |\psi|^2 = 2e|\psi|^2 v_s \tag{2–41}
\]

where \( v_s = (\hbar \nabla \phi - 2eA/c)/m^* \) is the velocity of the particle described by the pseudo-wavefunction \( \psi \). The free energy in the same limits is

\[
f = f_n + \left( \alpha + \frac{\beta}{2} |\psi|^2 + \frac{1}{2} m^* v_s^2 \right) |\psi|^2 + \frac{\hbar^2}{8\pi}. \tag{2–42}
\]

Minimizing the free energy with respect to \( |\psi| \) yields

\[
\alpha + \beta|\psi|^2 + \frac{1}{2} m^* v_s^2 = 0, \tag{2–43}
\]

which gives the solution

\[
|\psi|^2 = -\frac{\alpha}{\beta} \left( 1 - \frac{m^* v_s^2}{2|\alpha|} \right) = |\psi_\infty|^2 \left( 1 - \frac{m^* v_s^2}{2|\alpha|} \right). \tag{2–44}
\]

This says that the superfluid density decreases quadratically as the velocity \( v_s \) increases.

The supercurrent density Eq. (2–41) becomes

\[
J_s = 2e|\psi_\infty|^2 \left( 1 - \frac{m^* v_s^2}{2|\alpha|} \right) v_s. \tag{2–45}
\]
At \( v_s = \sqrt{2|\alpha|/3m^*} \), \( J_s \) has its maximum value as \( J_c \),

\[
J_c = 2e|\psi_\infty|^2 \frac{2}{3} \sqrt{\frac{2|\alpha|}{3m^*}} = \frac{4e\hbar|\psi_\infty|^2}{3\sqrt{3}m^*\xi} = \frac{cH_c}{3\sqrt{6}\pi\lambda},
\]  

(2–46)

where in getting the last two equalities Eqs. (2–31), (2–34), (2–35), and (2–36) are used. At current density higher than \( J_c \) there is no solution of \( v_s \) to Eq. (2–45); the thin film becomes normal. Hence \( J_c \) is called the critical current.

2.4.6.2 Parallel critical field

Apply an external magnetic field \( H \) parallel to the thin film surface. Take the direction normal to the film surface as \( z \) axis. We choose the London gauge so that the vector potential only has component \( A_x \approx Hz \). The phase \( \phi \) is constant in this gauge, making \( v_s = -2eA/m^*c \). By minimizing the Gibbs free energy of the film, it can be found that

\[
|\psi|^2 = |\psi_\infty|^2 \left( 1 - \frac{d^2H^2}{24\lambda^2H_c^2} \right).
\]  

(2–47)

Noting the proportionality between the gap \( \Delta \) and \( \psi \), the above equation means that low magnetic fields suppress the gap almost quadratically. The parallel critical field \( H_{c||} \) is defined as the value at which \( \psi \to 0 \),

\[
H_{c||} = 2\sqrt{6\frac{H_c\lambda}{d}}.
\]  

(2–48)

For a type II superconductor, \( \lambda \gg \xi \). Therefore \( \lambda \gg d \). The parallel critical field of a thin-film type II superconductor can be significantly higher than its thermodynamic critical field. Eq. (2–48) is valid as long as the film thickness \( d < \sqrt{5}\lambda \). Below this critical thickness, the magnetic transition to the normal state at \( H_{c||} \) is of second order; above it the transition becomes first order as in bulk samples. The transition becomes first order again for extremely thin samples with small spin-orbit scattering, in which the Pauli paramagnetism dominates over diamagnetism in the determination of the critical field, known as the Chandrasekhar-Clogston limit [44, 45].
2.4.6.3 Field distribution in parallel magnetic field

The field distribution $h(z)$ for a thin film in a homogeneous parallel magnetic field $H_a$ can be solved analytically. Here $h$ denotes the microscopic field, which distinguishes it from the spatially averaged macroscopic field $H$. The Ginzburg-Landau equations describe the local response. In the limit $|\psi|$ is constant they reduce to the London equations. Eq. (2–4) therefore applies, with the penetration depth given by Eq. (2–29). Assume that the thin film occupies the space from $z = -d/2$ to $z = d/2$. Solving Eq. (2–4) using the boundary conditions $h(-d/2) = h(d/2) = H_a$ yields

$$h(z) = H_a \frac{\cosh(z/\lambda)}{\cosh(d/2\lambda)}. \quad (2–49)$$

The macroscopic field $H$ can be found by averaging this $h$ over the film thickness,

$$H = \frac{1}{d} \int_{-d/2}^{d/2} h(z)dz = H_a \frac{2\lambda}{d} \tanh\frac{d}{2\lambda}. \quad (2–50)$$

This solution comes directly from London equations and the boundary condition, thus do not require $d \ll \xi$. However to require the field to be equal to the applied field $H_a$ at both surfaces, the sample should be thin enough so that the field is not disturbed at the interfaces. In the limit $d \ll \lambda$, one finds

$$H \approx H_a \left(1 - \frac{d^2}{12\lambda^2}\right). \quad (2–51)$$

The macroscopic field inside the thin film is therefore very close to the applied field.
CHAPTER 3
EXPERIMENTAL TECHNIQUES AND SAMPLES

3.1 Fourier Transform Infrared Spectroscopy

To obtain mid-infrared and far-infrared spectra, Fourier-transform infrared spectroscopy (FT-IR) can be used. It simultaneously detects all frequency, therefore is highly efficient compared to dispersive instruments (multiplex advantage). It has much higher throughput than conventional spectrometers requiring a slit aperture to achieve resolution (Jacquinot Advantage). It also provides measurements with high resolution.

3.1.1 Principles

The most crucial component of an FT-IR spectrometer is a Michelson interferometer, shown in Figure 3-1. A beam splitter bisects the incident collimated beam from the source. One branch of the beam is reflected towards a fixed mirror, and the other branch is transmitted towards a movable mirror oriented perpendicular to the fixed one. The two branches are reflected by the two mirrors and meet at the beam splitter with an optical path difference (or retardation) $\delta$ introduced by the movable mirror, resulting in interference. For a monochromatic source of wavenumber $\nu$ with intensity $I_\nu$, at an optical path difference $\delta$ the detected signal is

$$I'(\delta) = \frac{1}{2} I_\nu [1 + \cos (2\pi \nu \delta)].$$  \hspace{1cm} (3-1)

As the movable mirror changes $\delta$, the detected signal changes sinusoidally. When the two beams propagating to the detector interfere constructively, the detected signal is $I_\nu$, equal to the source intensity. When they interfere destructively, the detected signal is 0; all the incident power returns to the source. The oscillatory part of $I'(\delta)$ is defined as interferogram,

$$I(\delta) = \frac{1}{2} I_\nu \cos (2\pi \nu \delta).$$  \hspace{1cm} (3-2)

---

\[1\] For a detailed introduction to this technique, see for example Ref. [46]
In reality, the detected signal is always affected by beam splitter efficiency, detector response and amplifier characteristics. Incorporating these effects into Eq. (3–2) does not change the cosine term, but modifies its pre-factor $I_\nu$ to a new value denoted as $B(\nu)$. The practically detected interferogram is therefore

$$S(\delta) = B(\nu) \cos (2\pi\nu\delta). \quad (3–3)$$

The above equation can be readily generalized to the case of a broadband source,

$$S(\delta) = \int_{-\infty}^{+\infty} B(\nu) \cos (2\pi\nu\delta) d\nu. \quad (3–4)$$

The lower integration limit is extended to $-\infty$ for easier mathematical treatment. In reality $B(\nu)$ is understood to be zero for negative $\nu$. The Fourier-transform of Eq. (3–4) is the single-beam spectrum in the frequency domain,

$$B(\nu) = \int_{-\infty}^{+\infty} S(\delta) \cos (2\pi\nu\delta) d\delta. \quad (3–5)$$
Therefore, to obtain a single-beam spectrum is a two-step process: collect the interferogram and convert it to the frequency domain.

In reality it is impractical to scan the movable mirror over an infinitely long distance. The upper and lower limits of the integral in Eq. (3-5) are determined by the longest distance the movable mirror can travel, denoted as 0.5Δ. The corresponding optical path difference δ = Δ determines the finite resolution of the spectrum, Δν = 1/Δ, usually called nominal resolution. Another practical problem for measuring the interferogram is that it is impossible to obtain S(δ) at all values between −Δ and Δ. The interferogram can only be discretely sampled at finite increments. The challenge is to choose an optimal sampling method based on which the theoretical function can be unambiguously reconstructed. According to the Nyquist sampling theorem, the sampling rate should be at least twice of the bandpass of the spectrum. The Nyquist frequency is defined as half of the sampling rate. For example, if the spectrum is in the range between 0 and ν_{max}, a minimum sampling rate of 2ν_{max} is required, or equivalently the sampling interval should not be greater than 1/2ν_{max}. If the spectrum lies between ν_{min} and ν_{max}, the sampling interval should not be greater than 1/2(ν_{max} − ν_{max}). Moreover, any signal at frequency higher than the Nyquist frequency will be folded back into the sampling range if it is detected, causing aliasing. Electronic and optical filters should therefore be used to cut off the signal outside of the sampling range.

Typically, to obtain one spectrum the interferogram is sampled repeatedly, N times, to increase the signal-to-noise ratio, which is proportional to \(\sqrt{N}\). To add the interferograms coherently, corresponding points in the repeated interferograms must be sampled at the same retardation. The method for achieving this depends on the specific FT-IR spectrometer. The discussion that follows is specific to the Bruker 113. In this model, coherently adding interferograms is accomplished with the help of a secondary interferometer (Figure 3-1), which has its own beam splitter but shares the same scanner with the main interferometer. A white light generates an interferogram
with a narrow centerburst. Once this is detected, sampling is initiated. Instead of using the Nyquist frequency, in practice it is more convenient and accurate to use the interferogram of a helium-neon laser as the reference for sampling. This avoids the demanding tolerance on the scanner velocity for accurate sampling. The helium-neon laser, which is monochromatic at wavenumber \( \nu_{\text{HeNe}} = 15798 \text{ cm}^{-1} \), generates a sinusoidal interferogram detected independently by a Si photodiode. Sampling is triggered at every other zero crossing of the interferogram. This allows spectrum to be measured up to one half of the laser frequency, \( \nu_{\text{max}} = 7899 \text{ cm}^{-1} \), sufficient for the far-infrared and mid-infrared. Oversampling at every zero crossing doubles the upper limit to 15798 cm\(^{-1}\). In Bruker 66 this limit can be extended to about 47400 cm\(^{-1}\).

Once the interferogram \( S(\delta) \) is collected, it is converted to a single-beam spectrum through Fourier transform algorithms by a computer. For an accurate conversion, two complications have to be addressed.

Firstly, the finite retardation \( \Delta \) modifies Eq. (3–5) by a truncation function,

\[
B'(\nu) = \int_{-\infty}^{+\infty} S(\delta) \Pi(\delta) \cos(2\pi \nu \delta) d\delta = B(\nu) \ast f(\nu),
\]

where the boxcar truncation function \( \Pi(\delta) \) is unity for \(-\Delta \leq \delta \leq \Delta\) and 0 otherwise; \( f(\nu) \) is its Fourier-transform pair

\[
f(\nu) = 2\Delta \text{sinc}(2\pi \nu \delta).
\]

The last step in Eq. (3–6) is the result of the convolution theorem. The function \( f(\nu) \) has large sidelobes and can cause spectral leakage at those frequencies. To suppress the magnitude of these oscillatory sidelobes, a remedy is to use apodization functions instead of the boxcar function \( \Pi(\delta) \). A commonly used apodization function is the Norton-Beer function. Even though the apodization functions can bring an interferogram smoothly down to zero at the edge of the sampled region, the trade-off is the broadening of the lines and therefore the decreasing of the resolution.
Secondly, a phase correction has to be applied. This is to compensate for possible errors in determining the zero path difference, and for frequency-dependent errors induced by electronics and various optical components. These errors in combination result in a frequency-dependent phase error $\theta(\nu)$ in the interferogram,

$$S(\delta) = \int_{-\infty}^{+\infty} B(\nu) \cos[2\pi \nu \delta - \theta(\nu)] d\nu. \quad (3-8)$$

 Corrections are typically made by calculating the phase error $\theta\eta$ from the interferogram,

$$\theta(\nu) = \arctan \left[ \frac{\text{Im}(\tilde{B}'(\nu))}{\text{Re}(\tilde{B}'(\nu))} \right] \quad (3-9)$$

where Im and Re denote the imaginary and real parts of $\tilde{B}'(\nu)$, the complex Fourier transform of the interferogram. A widely-used scheme for phase correction is the Mertz method [47]. Using this method, the phase-corrected single-beam spectrum is

$$B''(\nu) = \text{Re}(\tilde{B}'(\nu)) \cos(\theta(\nu)) + \text{Im}(\tilde{B}'(\nu)) \sin(\theta(\nu)). \quad (3-10)$$

This is the final single-beam spectrum used in data analysis.

### 3.1.2 Sources in FT-IR

The commonly used infrared radiation source is high-temperature blackbody, modified by the material emissivity. Depending on the frequency range, different types of sources are used. Typically, high-pressure mercury lamp is used in the far-infrared (10–400 cm$^{-1}$). Globar (a resistively heated silicon carbide rod, operating at $\sim$1300 K) is used in the mid-infrared (400–4000 cm$^{-1}$). In the near-infrared (4000–12800 cm$^{-1}$), common sources are tungsten lamp and quartz-tungsten-halogen lamp [46].

The far-infrared region is especially difficult to cover by a blackbody source, because the spectral energy density decreases precipitously in the long-wavelength limit, according to Planck’s law. In principle, Globar can also be used in far-infrared spectroscopy. However its emissivity becomes too low below 100 cm$^{-1}$, where the mercury lamp is preferred [48]. The plasma of the mercury gas discharge can reach an effective temperature
of ~ 5000 K and has high emissivity. The plasma is enclosed in a quartz envelope which is opaque above ~100 cm$^{-1}$, making mercury lamp comparable to Globar in the far-infrared above 100 cm$^{-1}$ [49]. In the far-infrared, the radiance of synchrotron radiation can be three-orders-of-magnitude higher than conventional thermal sources, making it the best source for far-infrared spectroscopy [50].

Synchrotron radiation is light produced from relativistic electrons traversing the magnetic field in a synchrotron storage ring. The electrons circulate in the ring, producing sharp electric field pulses which give rise to broadband radiation. The radiation is extracted and carried to end stations around the storage ring, called beamlines, where experiments are performed. Although most synchrotron light sources are optimized to produce X-ray and vacuum ultraviolet radiation, radiation in the infrared region is much more intense than that from conventional thermal sources. Because the light originates from a small packet of electrons, the source can be treated as a point source. Thus, infrared light from a synchrotron can be easily collimated and focused to diffraction limited spot sizes, allowing high spatial resolution for infrared spectromicroscopy and high spectral resolution. Further more, the operating principles for the storage ring require the electrons to circulate in short bunches, thus the observed radiation at a given beamline is pulsed. This unique feature of the synchrotron allows timing measurements of typically nanosecond time scale, which is discussed in Section 3.2.2.

3.1.3 Detectors in FT-IR

Infrared detectors can be generally categorized into two types: thermal detectors and photon detectors. Due to fundamentally different types of noise occurring during the detector operation, these two classes of detectors have different detectivity characteristics. Photon detectors are favored in the near and mid-infrared spectral range, and thermal detectors are favored in the far-infrared. Good introductions to infrared detector operating principles and performance characteristics can be found in Refs. [51–53].
Thermal detectors operate by sensing the temperature change due to the heating from IR radiation. This temperature change induces changes in electrical conductivity, thermoelectric voltage or pyroelectric voltage, which are used to generate signal output. This type of detectors are fundamentally limited by temperature fluctuation noise arising from radiant power exchange with the surrounding background. Commonly used thermal detectors are doped silicon bolometers, doped germanium bolometers, and pyroelectric detectors such as DTGS (deuterated triglycine sulfate).

Photon detectors sense the electromagnetic radiation as photons instead of waves. They are mostly made of semiconductors, and are limited by generation-recombination noise arising from photon exchange with radiation background. In the mid-infrared, commonly used photon detectors include MCT (mercury cadmium telluride, HgCdTe) and InSb, but thermal detectors such as DTGS are also useful. In the near-infrared, a variety of photon detectors are available, e.g., InSb, InAs, Ge, InGaAs, InAs, PbSe, PbSe, and Si.

For the detection of far-infrared radiation, liquid-helium-cooled bolometers provide high sensitivity because the thermal and background fluctuation noise is significantly reduced when the bolometer element is cooled to the liquid helium temperature (4.2 K). The work discussed in this dissertation was mainly done in the far-infrared, using a doped-silicon bolometer from Infrared Laboratories. The helium reservoir can be pumped so that the liquid helium undergoes a phase transition to superfluid helium II at the lambda point (2.17 K). Continuous pumping reduces the operating temperature to 1.6 K, almost doubling the detectivity when compared to a bolometer designed to operate at 4.2 K [48]. The spectral response is limited by a far-infrared cut-on type filter at the entrance of the cone leading to the silicon element. This filter is cooled by the helium reservoir and significantly improves the detectivity.
3.2 Time-Resolved Infrared Spectroscopy

3.2.1 Principles

With the advance in ultrafast laser technology, time-resolved spectroscopy has become a powerful tool for the study of excitations in materials. In the simplest form, the pulse train from a laser is divided into two, one generating excitations in the sample manifested as changes in the sample’s spectral properties, and the other probing the induced changes. A controllable delay is introduced between the two pulse trains so that the sample’s spectral properties in the various phases of the relaxation back to the equilibrium state can be studied. This is called degenerate pump-probe spectroscopy. The technique can also be operated in a non-degenerate configuration, in which the pump and probe pulse trains come from different sources but are always synchronized. This adds the flexibility of probing the sample’s optical properties in the interested frequency range, which could be different from the laser frequency. The typically measured properties are the photo-induced changes in transmission, reflection, luminescence, Raman scattering, etc. The pulse width of the probe beam is usually the limiting factor of the time resolution, which determines the time scale of measurable dynamical processes. State-of-the-art femtosecond lasers make it possible to study dynamics of femto-second scale [54]. The technique proves to be a powerful tool to understand dynamical processes and excited-state properties of conventional superconductors [55–57] and to uncover the complex electronic structure and pairing mechanism in high-temperature superconductors [58–61].

3.2.2 Laser-Pump Synchrotron-Probe Spectroscopy at NSLS

The timing structure of synchrotron radiation allows laser pulses of high repetition rate to be synchronized to the synchrotron pulses from a storage ring to perform time-resolved pump-probe spectroscopy. We have access to such a pump-probe setup at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. A near-infrared laser excites the samples. The synchrotron radiation is used as the probe,
making use of the feature that pulse trains are radiated by electron bunches circulating in the ring. Though not appropriate for the study of ultrafast phenomena due to the limited time resolution, this laser-synchrotron system has a few advantages. The broadband nature of synchrotron radiation allows the probe beam to span an exceedingly wide frequency range. In the far-infrared, synchrotron radiation also has both brightness and power advantages over conventional thermal sources, increasing the sensitivity of the measurements. This section describes the laser system and the synchrotron facility at NSLS, as well as the technique of synchrotron-laser synchronization used in the time-resolved pump-probe experiment. Many descriptions in this section are from private correspondence with G. Lawrence Carr. Another source is Ref. [62].

### 3.2.2.1 Laser system

A Ti:sapphire laser from Coherent Laser Group is used to photo-excite samples. It has a tunable frequency range in the near-infrared from 700 nm to 950 nm. When mode-locked, it produces pulses of about 2 ps in duration and 20 nJ peak energy per pulse with a pulse repetition frequency (PRF) of 105.8 MHz. This laser is optically pumped by a continuous-wave Nd:VO$_4$ laser operating at 532 nm with a maximum power of 10.5 W. These two lasers are housed inside the U6 Beamline laser hutch, with an interlock system implemented to ensure safety of laser operations. The pulses from the Ti:sapphire laser are coupled into optical fiber cable using a standard fiber coupler, and transported to Beamline U4IR with the fiber ending several centimeters away from the window on the Oxford Magnet Cryostat. The light exiting the fiber diverges at a vertex angle of about 32°. A two-lens system is used to focus the laser beam onto the sample (Figure 3-2). The first lens (C) has a 30 mm focal length and approximately collimates the laser beam from the fiber. A second lens (F) with ~250 mm focal length then focuses the light at the sample location (G) in the magnet. When perfectly focused, the smallest spot size is about 0.5 mm. The lens tube with the second lens is held in a vacuum compression-type fitting. An AR coated BK-7 glass window (E) upstream of the second lens separates air from the
rough beam pipe vacuum. A focusing collar (A) on the fiber allows the distance from the fiber to the first lens to be adjusted, thus varying the focal distance inside the magnet. This enables us to defocus the laser spot to approximately fill the sample aperture, which is typically \( \sim 6 \) mm in diameter. The laser beam can be steered onto the sample using an X-Y stage (B) for the first lens. Polarizers can be placed in the square box (D) without affecting the focus because the beam is collimated between the two lenses. To ensure that the laser beam is directed to the sample and fill the sample aperture, a low-power red diode laser (0.95 mW, 670 nm) is used for visually aligning and focusing the beam before the optical fiber is affixed in front of the magnet window. The laser power can be measured in the U6 Laser hutch and at Beamline U4IR with a power meter. Due to coupling losses, the power delivered to the beamline is approximately 70\% of the input value.

3.2.2.2 VUV ring at NSLS

**Operation modes** The National Synchrotron Light Source has two storage rings, an X-ray ring and a VUV(vacuum ultraviolet) ring. Experiments presented in this dissertation were mostly performed at Beamline U4IR on the VUV ring. The electrons in the VUV storage ring are accelerated by radio-frequency (RF) cavities to restore their energy lost through synchrotron radiation. Due to the oscillation of the RF field,
only electrons arriving at some particular times are accelerated, resulting in electrons moving in bunches with bunch lengths ranging from \(\sim 1\) ns down to a few 10s of ps. The emitted synchrotron radiation is also pulsed as a consequence. The RF accelerating system operates at 52.9 MHz, making the minimum spacing between adjacent electron bunches 18.9 ns. The ring was designed to have a circumference of 51.0 m. With the operating energy of the ring at 808 MeV, electrons circulate around the ring almost at the speed of light. The orbiting period is therefore 170 ns. This provides 9 equally-spaced locations, each one known as an “RF bucket”, where electron bunches can exist and receive the proper acceleration to remain on a stable orbit. The VUV ring electron injection system can fill specific RF buckets, allowing for different bunch patterns. Moreover, the bunch length, which determines the pulse width of synchrotron radiation, can be controlled by a second higher frequency RF system, by adjusting the ring magnet system, or by adjusting the electron beam energy. The filling pattern for normal operation is a train of 7 bunches of approximately equal-current followed by two empty RF buckets. This mode allows the highest average current of 1 A immediately after injecting electrons into the ring, which is the most stable and meets most users’ requirements. The pulse width is 1.2–2.4 ns and the PRF is 52.9 MHz.\(^2\) Special modes of operations can be achieved, with different filling patterns and bunch lengths. For example, two other operation modes having the same filling pattern and PRF as the normal mode are the 7-bunch detuned mode with 800 mA of maximum average current and 0.6–1.0 ns of pulse width, and the 7-bunch compressed mode with 200 mA maximum average current and 300–500 ps of pulse width. These special operations, though having lower intensity than the normal mode, provide better time resolution critical in a time-resolved experiment. The ring can also be operated at

\(^2\) In fact two bunches are empty in this mode and other 7-bunch modes, so that there are no synchrotron pulses emitted from them. But the pump-probe experiment is not affected, because 2 out of the 9 laser pulses synchronized to the synchrotron pulses are simply not used in the experiment.
a 3-bunch symmetric mode with a PRF of 17.6 MHz and pulse width of 0.7–1.4 ns, and
at a 1-bunch mode with a single RF bucket filled, so that the PRF is 5.9 MHz, again
with lower average current. These other fill patterns are useful in the study of dynamical
processes of longer time scale.

**Beamline U4IR** Our work was done at Beamline U4IR of the National Synchrotron
Light Source. At long wavelength, the emission angle of synchrotron radiation is large,
making the extraction of infrared beam difficult. Unique extraction optics (90 mrad
horizontal × 90 mrad vertical) at U4IR offers high-brightness beams in mid and
far-infrared regions, almost 100–1000 times brighter than conventional sources [63].
Moreover, in the far-infrared beyond 100 cm$^{-1}$ synchrotron radiation has higher power
than thermal sources [63]. In the far-infrared, the spot size of the beam is diffraction
limited (approximately 8 times of the wavelength at the sample location, after demagnified
by the optical system focusing the infrared beam into the magnet). Above 1000 cm$^{-1}$
the VUV source is no longer diffraction limited, and the physical electron beam size
controls the source size. The beamline has two parts: an ultra-high vacuum (UHV)
section that is directly connected to the storage ring including the extraction optics, and
a rough vacuum section containing optics that directs light to the spectrometer. The
two sections are separated by a diamond window, which is mostly transmissive from the
far-infrared to near ultra-violet. The beamline covers the energy range from 2 meV to
2.5 eV (20–20000 cm$^{-1}$). A combination of beam splitters and detectors in principle allows
FT-IR in the whole infrared range. An Oxford Spectromag 10 T magnet is available for
magnetic studies. The incident beam passes through two Z-cut crystal quartz windows.
The first window (6 mm thick) separates the rough beam pipe vacuum from the cryostat
high vacuum. The second window (~1 mm thick) separates the high vacuum from the
VTI sample space. These quartz windows [64] on the magnet and the cooled filter in
the bolometer limit the usable far-infrared range to be blow ∼110 cm$^{-1}$. The light is
Figure 3-3. Experimental set-up for laser-pump synchrotron-probe spectroscopy at NSLS. If the divide-by-N pulse picker and its electronic drive are used, the bunch timing signal frequency and the PRF of the output laser pulses from the pulse picker are different from those shown in the figure.

predominantly vertically polarized as it enters the magnet, especially at low frequency below 50 cm⁻¹.

3.2.2.3 Timing scheme and synchronization

The laser and synchrotron pulses need to be synchronized and an adjustable delay is introduced between the two in a laser-pump synchrotron-probe experiment. The set-up and the timing scheme are illustrated in Figure 3-3 and Figure 3-4, respectively. Details of how the system works are explained below.

To synchronize the laser and synchrotron pulses, a reference signal generated from the synchrotron ring is sent to the laser control system in U6 laser hutch. Specifically, a
Figure 3-4. Timing scheme for laser-pump synchrotron-probe spectroscopy at NSLS. The ratio meter accounts for the drift in the detected signal due to the decay of the synchrotron ring current, by constantly monitoring the beam current and dividing out the drift. ConOptics 360-40 EOM and ConOptics 350-160 EOM are the divide-by-2 and divide-by-N pulse pickers; ConOptics Model 10 and ConOptics Model 25D are their drive electronics. ConOptics Model 305 Countdown or HP 8082A controls the electronic drive ConOptics Model 25D. The output from Photodiode 1 is used in the Synchro-lock system. Photodiode 2 is for monitoring the laser pulses before they are coupled to the optical fiber cable, which delivers them to photo-excite samples.
bunch timing signal is generated from a stripline electrode in a short straight section of the storage ring. The electric field of each passing bunch of electrons generates a voltage signal in the stripline that is sent to electronics for turning each bunch signal into a constant amplitude pulse. Two sets of pulse signals are produced: one is a pulse for each electron bunch in the bunch train with the PRF depending on the operation mode, and the other is a single pulse for the full orbit with a PRF of 5.9 MHz. The 5.9 MHz single pulse is derived from one particular electron bunch in the ring, which exists for all modes of operations including the 1-bunch mode. The corresponding pulse signal is therefore called “1-bunch clock signal” even when other RF buckets are filled. It is used in the synchronization process when the synchrotron ring is operated in the 1-bunch mode and in all 7-bunch modes. For the 3-bunch symmetric mode, the actual bunch signal with a PRF of 17.6 MHz is used. Since this mode was not used in our experiment, the following descriptions focus on the scheme with the 1-bunch clock signal as the reference.

The 1-bunch clock signal is sent to an HP 81101 pulse generator, which drives the pulse generator’s trigger. A new pulse is generated according to the time-delay setting on the pulse generator. The output pulse is sent to U6 laser hutch where it is divided by a power splitter. One part goes to the divide-by-N pulse picker electronics. The other part goes to a 52.9 MHz narrow band pass filter that separates out the 9th harmonic of the 5.9 MHz pulse train, which matches precisely the RF frequency. A RF amplifier boosts the 52.9 MHz signal so that it can be split in two, with one part going to the divide-by-2 pulse picker and the other serving as the reference for the Coherent “Synchro-lock” system for synchrotron-laser synchronization. The Synchro-lock system mixes the pulsed laser output signal detected by a photodiode (Photodiode 1 in Figure 3-4) with the reference signal. An error signal is produced to correct the cavity length of the Ti:sapphire laser, which determines the laser PRF. A stepper motor on the cavity end mirror, a glass prism pair on a galvanometer movement, and a piezoelectric transducer on one of the cavity fold mirrors work together to minimize this error signal. The Synchro-lock system is of a phase-locked
loop type, so that when the error signal is reduced to zero the laser pulses are not only at the exact same repetition frequency, they also have a fixed (and controllable) time delay relative to the synchrotron pulses. The accuracy of the synchronization can be checked by placing a high-speed photodiode at the sample location at Beamline U4IR to simultaneously detect the synchrotron and laser pulses. A fast oscilloscope is used to display the signal output for diagnosis.

The PRF of the Ti:sapphire laser is 105.8 MHz, twice of the ring RF system frequency. Laser pulses have to be selected to match the bunch patterns of the synchrotron radiation. This is achieved by using pulse pickers from ConOptics, which are electro-optic modulators (EOMs) made of Pockels cells. The Pockels cell is basically a voltage-controlled optical retarder combined with a linear polarizer. The laser light is linearly polarized along the horizontal direction when it enters the cell. At one particular voltage, the Pockels cell acts as a half-wave plate that converts the polarization to vertical and the laser light is rejected by the linear polarizer; at another voltage the cell acts as a full-wave plate and the polarization is unaffected, thus the laser light comes through. The pulse picking process is controlled by varying the voltage applied to the cell between these two voltage settings. To match the 52.9 MHz PRF of the 7-bunch modes, a divide-by-two pulse picker (ConOptics 360-40 EOM) is used to select every other laser pulse. The electronic drive for this pulse picker, ConOptics Model 10, takes in a 52.9 MHz reference signal, and then uses a RF amplifier and a DC power supply to alternate the output voltage between the two switching voltages at that frequency. A divide-by-N pulse picker (ConOptics 350-160 EOM) is used to match the bunch patterns when the ring is operated at other modes. For example, the 1-bunch mode requires the divide-by-N pulse picker to operate as divide-by-9. The electronic drive ConOptics Model 25D works similarly as ConOptics Model 10, but its operation requires an input from an additional pulse generator, ConOptics Model 305 Countdown (only works for symmetric modes) or HP 8082A (works for any modes), which sets the voltage pulse pattern used by the drive
according to the synchrotron operation mode. In either case, all rejected pulses are recovered, delayed, adjusted to restore the original polarization, and re-introduced into the pulse train from the laser.

The HP 81101 pulse generator sets an adjustable delay between the laser and synchrotron pulses, therefore serves as a programmable variable delay. When it shifts the reference pulse signal by certain delay time, both the laser and the divide-by-2 pulse picker (or the divide-by-N pulse picker if it is used) shift together. For the laser pulses to be optimally transmitted or maximally rejected, they have to arrive at the pulse picker at the correct moment when the voltage on the pulse picker just changes to one of the two operating values. For the divide-by-2 pulse picker this can be achieved by adjusting the pulse delay of the laser on the Synchro-lock electronics software. For the divide-by-N pulse picker a delay can be set on the pulse generator (ConOptics Countdown Model 305 or HP 8082A) that controls the electronic drive. When all these are successfully done, laser pulses with correct time structure are synchronized to the synchrotron pulses, with a controllable time delay between the two.

3.2.2.4 Differential technique

To improve sensitivity and single out the signal due to the time-dependent change of the sample properties, a differential technique is employed in the data acquisition process. The SRS 830 lock-in amplifier’s internal oscillator introduces a phase modulation on the HP 81101 pulse generator’s trigger signal through a bias-tee, see Figure 3-4. This sinusoidally dithers the arrival time $t$ of the laser pulse with respect to the synchrotron pulse with a small amount $dt$, which is set to be slightly smaller than the synchrotron pulse width. The modulation signal also serves as the reference for the lock-in amplifier, which detects the signal as the difference in the sample response at the time $t - dt/2$

---

3 The DC bias tee passes the high-frequency RF signal with a DC offset supplied from the lock-in amplifier, with minimum disturbing in the RF signal.
and \( t + dt/2 \). When \( dt \) is sufficiently small, the detected signal is a derivative signal of the sample response, denoted as \( dS/dt \). Integrating it over time, we obtain the sample response \( S(t) \).

### 3.3 Sample Parameters

We started with a set of NbTiN and NbN thin films of varying thicknesses and substrate materials, and selected one NbTiN film on quartz substrate and one NbN film on MgO substrate for our magnetic-field study. A selection criteria was strong spin-orbit scattering \( \hbar/\tau_{so} \Delta \gg 1 \) [65], where the spin-orbit scattering time \( \tau_{so} = 3.0 \times 10^{-14} \text{ s} \) is taken to be that of NbTi [66] and \( \Delta \) is the single-particle gap. The NbTiN film was grown by reactive magnetron sputtering in argon and nitrogen gas with a NbTi cathode, and the NbN film by reactive sputtering of Nb in N\(_2\) atmosphere [67]. Table 3-1 lists the sample parameters, including the film thickness \( d \), optical gap \( \Delta_0 \), critical temperature \( T_c \), sheet resistance \( R_\square \) at 20 K, penetration depth \( \lambda \), coherence length \( \xi \), zero-temperature parallel upper critical field \( H^{\parallel}_{c2,0} \), zero-temperature perpendicular upper critical field \( H^{\perp}_{c2,0} \), and the refractive index of the substrate \( n \). Determination of some of these parameters will be presented in the following sections. The optical gap is determined from the optical data to be discussed in Section 4.4.2.

The quartz and MgO substrates have negligible absorption in the spectral range of interest (10–110 cm\(^{-1}\)). Both materials have their refractive indices almost independent of frequency in this spectral range. For quartz \( n \) is about 2.123 at 300 K and 2.119 at 1.5 K [68], showing very weak temperature dependence. We use a constant value of 2.12 below 20 K. The refractive index of MgO below 10 K is not directly available in literature, but we found it varies from 2.78 at 20 K to 2.72 at 50 K in one study [69], and from 3.09 at 10 K to 3.10 at 65 K in another [70]. Both studies indicate weak temperature dependence below 65 K, though the absolute values from them are different. We choose an intermediate value of 2.90 as the refractive index of MgO between 2 K and 20 K.
Table 3-1. Sample parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d$ (nm)</th>
<th>$\Delta_0$ (cm$^{-1}$)</th>
<th>$T_c$ (K)</th>
<th>$R_\square$ (Ω)</th>
<th>$\lambda$ (nm)</th>
<th>$\xi$ (nm)</th>
<th>$H_{c2,0}^\parallel$ (T)</th>
<th>$H_{c2,0}^\perp$ (T)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbTiN/quartz</td>
<td>10</td>
<td>12.8</td>
<td>10.2</td>
<td>117</td>
<td>200-400</td>
<td>3.8-5.0</td>
<td>22.02</td>
<td>12.50</td>
<td>2.12</td>
</tr>
<tr>
<td>NbN/MgO</td>
<td>70</td>
<td>17.9</td>
<td>12.8</td>
<td>48</td>
<td>180-500</td>
<td>4.0-7.0</td>
<td>21.83</td>
<td>49.55</td>
<td>2.90</td>
</tr>
</tbody>
</table>

3.3.1 Critical Temperature

To determine the critical temperature of both samples, we performed four-probe resistivity measurements at Station SCM2 at the National High Magnetic Field Laboratory. A 2 mm × 2 mm piece was cut from each sample for such measurements because of the requirements of the experimental set-up. Electrical contacts were made by gluing gold wires to the thin films with silver paint. The two samples were mounted simultaneously on a rotating probe which allows accurate alignment of the sample surface with respect to the magnetic field orientation. Resistivity was measured from 300 K down to 5 K, shown in Figure 3-5. If the critical temperature is defined as the temperature at which the resistance drops to zero, we estimate $T_c$ to be about 10.2 K for NbTiN and 12.8 K for NbN.

![Resistance vs temperature for NbTiN and NbN from four-probe resistivity measurements. $T_c$, if defined as the temperature at which the resistance drops to 0, is about 10.2 K for NbTiN and 12.8 K for NbN.](image-url)
3.3.2 Normal-State Sheet Resistance

The normal-state sheet resistance \( R_{\square} = 1/\sigma_n d \), where \( \sigma_n \) is the normal-state optical conductivity, can be determined from the normal-state transmittance. In Eq. (C–29) in Appendix C, setting \( \sigma_1 = \sigma_n \) and \( \sigma_2 = 0 \), and inverting the equation, we have

\[
R_{\square} = \frac{Z_0}{\sqrt{4n/T_n - n - 1}}, \tag{3–11}
\]

where \( T_n \) is the normal-state transmittance at normal incidence, and \( Z_0 \approx 377 \, \Omega \) is the vacuum impedance. In getting Eq. (3–11) we made the assumption that the scattering rate \( 1/\tau \) is much greater than the far-infrared frequency, so that the Drude conductivity

\[
\sigma_n = \frac{\sigma_{n,0}}{1 - i\omega\tau} \tag{3–12}
\]

can be approximated as its dc value \( \sigma_{n,0} \).

To determine their normal-state sheet resistance, the two samples were mounted on sample holders and loaded into an Oxford magnet, then cooled to 20 K in helium vapor at which transmission was measured. An empty sample holder of the same size was measured as the reference to calculate transmittance. The data are shown in Figure 3-6. The normal-state transmittance for both samples is flat in the far-infrared, at a level of about 0.211 for NbTiN and 0.083 for NbN. This flat behavior confirms that \( \omega\tau \ll 1 \) is a valid assumption for both samples in the far-infrared. Using the value of \( n \) in Table 3-1, \( R_{\square} \) is calculated to be 117 \( \Omega/\square \) for NbTiN and 48 \( \Omega/\square \) for NbN. When comparing these values with those obtained from the resistivity data shown in Figure 3-5, we found a good agreement for NbTiN, but a big discrepancy for NbN. We repeated the optical measurements two more times and reproduced \( R_{\square} \) within a difference of 10%, but did not have a chance to repeat the four-probe resistivity measurement. Therefore we use the \( R_{\square} \) values listed in Table 3-1 in our analysis. The discrepancy for NbN might be due to the change of contact resistance during the cooling process.
Figure 3-6. Normal-state transmittance of NbTiN and NbN at 20 K, measured with a resolution of 4 cm$^{-1}$. The solid lines indicate the average of the data points, which is 0.211 for NbTiN and 0.083 for NbN.

3.3.3 Penetration Depth and Coherence Length

There is a great amount of literature on the penetration depth and coherence length of NbN thin films grown by different methods under different conditions. For example, the approximate values of the penetration depth (mostly at low temperature) were reported as 200 nm by Shapoval et al. [71], 187 nm by Kawakami et al. [72], to be consistently greater than 300 nm at 10 K by Hu et al. [73], 270 nm by Villegier et al. [74], 400 nm by Feenstra et al. [75], 194 nm by Komiyama et al. [76], 400 nm by Pambianchi et al. [77], 370 nm by Oates et al. [78], 280-380 nm by Stern et al. [79], and 300-500 nm by Kubo et al. [80]. The coherence length was reported to be about 5 nm by Chockalingam et al. [81], 4.3 nm by Thakur et al. [82], 4.0 nm by Bell et al. [83], 6.9 nm by Shoji et al. [84], and 4-7 nm by Irie et al. [85]. In summary the penetration depth of NbN is between 180 nm and 500 nm, and the coherence length is between 4 nm and 7 nm.

For the similar compound NbTiN, the penetration depth at low temperature was determined to be 200-400 nm and coherence length to be 4 nm by Yu et al. [86]. In another study Yu et al. determined the coherence length to be 3.8 nm [87]. Kau et al. [88]
found the coherence length to be 5 nm. The reported value of coherence length is therefore between 3.8 nm and 5.0 nm.

3.3.4 Critical Fields

$H_{c1}$ for both samples is low, at least below 1 T, which is the lowest applied field we use in our study. Mathur et al. [89] reported $H_{c1}$ to be 4 mT for NbN thin film and 9.3 mT for a bulk sample at 4.2 K. According to Lamura et al. [90] $H_{c1}$ should be less than 200 mT at temperature close to zero. $H_{c2}^\parallel$ and $H_{c2}^\perp$ at various temperatures are determined from four-probe resistivity measurements, shown in Figure 3-7 and Figure 3-8, respectively. Well below the critical temperature, the resistance was measured by scanning the magnetic field between 0 T and 16 T at selected temperatures. Close to the critical temperature, the resistance was measured by sweeping temperature between 5 K and 20 K at selected low field values. Since the transition is broad, for convenience we assume that the transition occurs when the resistance drops to 1/2 of its 20 K value.

To estimate the value of $H_{c2}^\parallel$ at low temperature, which is beyond the measurement range, the data points are fitted to the form

$$H_{c2}^\parallel = H_{c2,0}^\parallel \sqrt{\frac{1 - t^2}{1 + t^2}}, \quad (3-13)$$

where $t = T/T_c$ is the reduced temperature. The above equation is based on the fact that for a thin film superconductor of thickness $d$, $H_{c2}^\parallel = 2\sqrt{6}H_c\lambda/d$ according to Eq. (2–48), where the thermodynamic critical field $H_c \propto 1 - t^2$ and the penetration depth $\lambda \propto 1/\sqrt{1 - t^4}$ given by Eqs. (2–33) and (2–6). For NbTiN, the fit yields $H_{c2,0}^\parallel \approx 22.02$ T and $H_{c2}^\parallel \approx 20.25$ T at 3 K. For NbN, the fit yields $H_{c2,0}^\parallel \approx 21.83$ T and $H_{c2}^\parallel \approx 21.30$ T at 2 K.

The temperature dependence of $H_{c2}^\perp$ has a different form. According to Eq. (2–40) $H_{c2}^\perp \propto H_c^2\lambda^2$, and assuming the same temperature dependence of $H_c$ and $\lambda$ mentioned in
Figure 3-7. Four-probe resistivity data in parallel fields for NbTiN (first row) and NbN (second row). Left column: resistance vs parallel field at different temperatures. Middle column: resistance vs temperature at different parallel fields. Right column: circles are $H^\parallel_{c2}$ extracted from data; solid lines are fits using Eq. (3–13). In the first two columns the dashed lines indicate the resistance at 20 K and a half of that value.

In the previous paragraph, we have

$$H^\perp_{c2} = H^\perp_{c2,0} \frac{1 - t^2}{1 + t^2}. \quad (3–14)$$

Using this equation to fit the data, we found $H^\perp_{c2,0} \approx 12.50$ T for NbTiN and $H^\perp_{c2,0} \approx 49.55$ T for NbN.

The extracted values show that for NbTiN $H^\parallel_{c2} > H^\perp_{c2}$, while for NbN $H^\parallel_{c2} < H^\perp_{c2}$. This can be explained by Eq. (2–40) and Eq. (2–48), $H^\parallel_{c2}/H^\perp_{c2} = 2\sqrt{3}\xi/d$. Using the values of $d$ and $\xi$ in Table 3-1, $H^\parallel_{c2}/H^\perp_{c2} \approx 1.5$ for NbTiN and $H^\parallel_{c2}/H^\perp_{c2} \approx 0.3$ for NbN, which is qualitatively consistent with the critical fields found by four-probe resistivity
Figure 3-8. Four-probe resistivity data in perpendicular fields for NbTiN (first row) and NbN (second row). Left column: resistance vs perpendicular field at different temperatures. Middle column: resistance vs temperature at different perpendicular fields. Right column: circles are $H_{c2}^\perp$ extracted from data; solid lines are fits using Eq. (3–14). In the first two columns the dashed lines indicate the resistance at 20 K and a half of that value.

measurements. One previous study of a 200 nm NbN thin film found $H_{c2,0}^\parallel \approx 32$ T and $H_{c2,0}^\perp \approx 44$ T [91].
CHAPTER 4
MAGNETO-SPECTROSCOPY OF PAIR-BREAKING EFFECTS

4.1 Magnetic-Field-Induced Effects on Superconductivity

Magnetic fields have dramatic effects on the superconducting state; when they are stronger than the upper critical field, superconductivity is destroyed. Fields below this critical value act on the spin and orbital motion of quasiparticle states.

An applied field lifts the spin-degeneracy of each electronic state, potentially causing a Pauli paramagnetic shift of quasiparticle density of states $[14, 92]$ which would give a linear shift of the spectroscopic gap with field $[93]$. The effect is noticeable only for materials with a very small spin-orbit scattering rate, in which the spin is a “good” quantum number. In the pure Pauli limit where the effect of the magnetic field on the electron orbital motion can be ignored, Clogston $[44]$ and Chandrasekhar $[45]$ proposed that a transition to the normal state should occur at a critical field when the Zeeman splitting of the Cooper pairs becomes larger than the superconducting condensation energy. The transition is of first order, and the critical field is given as $H_p = \Delta_0 / \sqrt{2}\mu_B$.

In certain materials in which the Pauli paramagnetism dominates, when the field is strong enough, a phase called the Fulde-Ferrel-Larkin-Ovchinnikov (FFLO) state can exist, in which Cooper pairs are formed with non-zero total momentum and the order parameter is spatially inhomogeneous $[94, 95]$.

The field also alters the orbitals of single-particle states from which the BCS ground state is formed, breaking the time-reversal symmetry of the condensate pairing. The result is a finite lifetime for a given Cooper pair and an overall weakening of the superconducting state. This weakening is directly revealed by a reduction in the single-particle gap and forms the basis of the pair-breaking theory originally proposed by Abrikosov and Gor’kov $[96, 97]$ to describe the effect of magnetic impurities on superconductivity. The depairing phenomena can be characterized by a single pair-breaking parameter, $\Gamma$, that depends on whether the theory describes external magnetic fields, supercurrents, spin exchange,
or other effects. Maki [98] showed that a thin film superconductor in the dirty limit will exhibit pair breaking, equivalent to that caused by magnetic impurities, when subjected to a homogeneous magnetic field. He also demonstrated that for a thin film type-II superconductor in the vortex state, the field-induced perturbation causes spatial variation of the order parameter, which gives rise to another distinct type of pair breaking [5].

In general, both paramagnetism and orbital pair breaking can affect the spectroscopic gap. However the Pauli paramagnetism is “smeared out” in materials with large spin-orbit scattering [65], making the orbital effect dominant. If the sample is of the form of a thin film, the film thickness also determines the spin and orbital depairing regimes. As the film thickness is decreased, the electron orbital motion becomes more compressed. The orbital effects of the screening current gives way to the spin Pauli paramagnetism [93, 99, 100], at a threshold thickness, e.g., approximately 10 nm for aluminum films.

4.2 Motivation

Optical spectroscopy probes directly a superconductor’s excitation spectrum, making it ideal for studying the gap evolution under an applied magnetic field. Ordinary metallic superconductors have a gap in their optical spectrum [34], requiring a minimum of 2\(\Delta\) of photon energy to break Cooper pairs. As discussed in Section 2.3.6, the gap makes the \(T = 0\) real part of the optical conductivity be zero for photon energies below the gap. The missing spectral weight in \(\sigma_1(\omega)\) appears as a delta function at zero frequency. By the Kramers-Kronig relations, the delta function gives a dominant \(1/\omega\) form to \(\sigma_2(\omega)\). By determining both the real and imaginary parts of the field-dependent optical conductivity, one can test theories for the magnetic field suppression of the gap.

We find it somewhat surprising that magnetic-field-induced pair-breaking effects have not been convincingly verified by optical studies. Such effects have been observed in tunneling spectra [101] and are hinted at by absorption data [93]. In addition, the effect of magnetic impurities have been studied in detail [102, 103]. In this chapter we report far-infrared transmission and reflection spectra of NbTiN and NbN under external
magnetic field, applied parallel to the film surface. The extracted optical conductivity \( \sigma_1 \) demonstrates a suppression of the gap by the field, in quantitative agreement with pair-breaking theory. This is the first time that optical absorption has been employed to test quantitatively the theory of pair breaking by an external magnetic field.

### 4.3 Experimental

We would like to determine the optical gap from the optical conductivity, which can be extracted from transmission and reflection. Infrared transmission and reflection measurements were performed at Beamline U4IR of the National Synchrotron Light Source, Brookhaven National Laboratory, using high-brightness broadband synchrotron radiation as the spectroscopic source. The samples were mounted in a \(^4\)He Oxford cryostat equipped with a 10 Tesla superconducting magnet. The spectra were collected using a Bruker IFS 66-v/S spectrometer and a high sensitivity, large area composite Si bolometer operating at 1.6 K. Cooled filters in the bolometer and the quartz window on the magnet limited the upper frequency to 110 cm\(^{-1}\).

#### 4.3.1 Consideration of Field Orientation

The field direction is important when considering the behavior of these type II superconductors. For field perpendicular to thin-film samples, vortices appear above \( H_{c1} \) and form a dense lattice of lossy core material as it approaches \( H_{c2} \). We intended to avoid this vortex regime by orienting the field parallel to the film surface.

In the case of NbTiN, because the film thickness is much smaller than the penetration depth and somewhat close to the coherence length, a significant density of vortices is unlikely. Consider the possibility of the presence of vortices. Assuming a triangular vortex lattice, the vortex spacing \( a_\Delta = 1.075 \sqrt{\Phi_0/H} \) is 48.9 nm at 1 T and 15.5 nm at 10 T. Even at the highest applied field of 10 T the vortex spacing is larger than the film thickness. Therefore we do not expect vortex-induced effects to be significant. In addition,
Figure 4-1. Sample holders for transmission and reflection measurements in parallel magnetic fields. The sample is the thin black slab near the middle. The arrowed lines show the path of the beams. The left holder is used for transmission measurement at normal incidence. The middle one is for transmission at 30° angle of incidence. The right one is for reflection at 30° angle of incidence. The screws on top are used to attach the sample holders to a probe that goes into the magnet.

According to Eq. (2–51) the average magnetic field in the film is approximately

$$H \approx H_a \left( 1 - \frac{d^2}{12\lambda^2} \right) \approx 0.999H_a,$$

where $H_a$ is the applied field. Hence, the field is nearly uniform in the thin film and almost the same as the applied field.

The NbN film is much thicker than NbTiN. Even at 1 T it is unlikely to avoid the presence of vortices. However the average field inside the thin film is more than 0.987 of the applied field according to Eq. (2–51). The field is therefore nearly homogeneous and equal to the applied field.

We designed special sample holders to measure transmission and reflection in a parallel field.¹ Sketches are shown in Figure 4-1. For the NbTiN sample, the angle of incidence in the transmission measurement was near normal, shown in the left panel of

---

¹ The sample holders for transmission measurement at normal incidence and reflection measurement at 30° angle of incidence were designed by G. Lawrence Carr and Jungseek Hwang. The sample holder for transmission measurement at 30° angle of incidence was designed by the author.
Figure 4-1: a polished aluminum mirror reflects the input beam vertically onto the sample, and another mirror directs the transmitted beam back to the original direction at an elevated level. The angle of incidence in the reflection measurement was about 30°, shown in the right panel of Figure 4-1: a polished aluminum roof-type mirror reflects the input beam onto the sample at a 30° angle and then redirects the reflected beam back onto the original optical path. To analyze data, the reflection needs to be corrected for the 30° angle of incidence.

We began studying the NbN sample after the analysis of the NbTiN sample was completed. During the analysis we realized that we can match the angle of incidence in both transmission and reflection measurements. When measuring transmission for NbN, we modified the transmission sample holder, shown in the middle panel of Figure 4-1, so that the angle of incidence was also 30°.

4.3.2 Transmission and Reflection in Parallel Field

Our goal is to extract the optical conductivity of the thin film superconductors from reflection and transmission measurements. Beginning with the pioneering work of Palmer and Tinkham [36], this approach has been used a number of times to study both metallic and cuprate superconductors [104, 105]. In a conventional transmittance or reflectance measurement, one measures separately the sample and a reference having known optical properties—typically an open aperture with no sample for transmittance and a known metal for reflectance. Sample exchange can lead to errors, especially for the absolute reflection, where sample orientation is critical. To avoid sample exchange errors, we used the sample in the normal state, and at $H = 0$ T, for our reference. Specifically, we measured the sample spectrum (transmission or reflection) at different fields ranging from 0 to 10 T in the superconducting state ($T = 3$ K for NbTiN and $T = 2$ K for NbN), using the normal state ($T = 20$ K), zero-field spectrum for the reference. The relative measurements can be made absolute by measuring the normal-state transmittance and reflectance or by calculating them from the Drude model in the limit $\omega \ll 1/\tau$, a very
good assumption for our films as the measured normal-state transmittance is almost constant in the measured frequency range (Figure 3-6). The directly acquired data are therefore the ratios of transmittance $T_s/T_n$ and reflectance $R_s/R_n$, where the subscripts $s$ and $n$ denote superconducting state and normal state respectively. Figure 4-2 shows the data at various fields. The NbTiN was measured with a resolution of $3.5$ cm$^{-1}$, which does not fully resolve the interference fringes from multiple reflections inside the substrate. The NbN was measured with a resolution of $4$ cm$^{-1}$. The peak in $T_s/T_n$ shifts to lower frequency as field increases, suggesting the suppression of the energy gap due to the field.

For NbTiN, the reflection data were corrected for the measured stray light and for the $30^\circ$ angle of incidence (Appendix D) before calculating the optical conductivity.

### 4.4 Analysis

#### 4.4.1 Extraction of Optical Conductivity

The analysis for the thin film optical conductivity $\sigma = \sigma_1 + i\sigma_2$ of NbTiN begins with the expressions for the normal-incidence transmission through, and reflection from, the front film surface of the sample [36],

$$T_s = \frac{4n}{(Z_0\sigma_1 d + n + 1)^2 + (Z_0\sigma_2 d)^2},$$

$$R_s = \frac{(Z_0\sigma_1 d + n - 1)^2 + (Z_0\sigma_2 d)^2}{(Z_0\sigma_1 d + n + 1)^2 + (Z_0\sigma_2 d)^2},$$

where $Z_0 \approx 377$ Ω is the vacuum impedance, $d$ is the film thickness, and $\sigma_1, \sigma_2$ are the real and imaginary parts of the optical conductivity of the thin film in the superconducting state (thin film optics is discussed in detail in Appendix C). The normal-state transmittance and reflectance can be derived from Eqs. (4-2) and (4-3) by setting $\sigma_1 = \sigma_n$ and $\sigma_2 = 0$ because $\omega \ll 1/\tau$ in the far-infrared,

$$T_n = \frac{4n}{(Z_0\sigma_n d + n + 1)^2};$$

$$R_n = \frac{(Z_0\sigma_n d + n - 1)^2}{(Z_0\sigma_n d + n + 1)^2}. $$

64
Figure 4-2. Measured superconducting-state to normal-state ratios of transmission $T_s/T_n$ and reflection $R_s/R_n$ at various parallel magnetic fields. The weak oscillatory features shown in the NbTiN data are partially-resolved multiple internal reflections in the substrate. $\theta_i$ is the angle of incidence.

Here $\sigma_n$ is related to the normal-state sheet resistance of the thin film $R_{\square} = 1/\sigma_n d$, which we have determined from the normal-state transmittance.

In practice, we measure the combination of film and substrate, giving the external transmittance $T_{\text{ext}}$ and external reflectance $R_{\text{ext}}$. If the substrate surfaces are parallel on the scale of the wavelength and the measurement resolution is high enough, these quantities typically show fringes due to partially coherent multiple internal reflections inside the substrate. A typical spectrum measured with high resolution is shown in Figure C-4 in Appendix C. Smoothing high resolution data or taking measurements with a low resolution produces the incoherent spectrum, where one may add intensities rather
than amplitudes. In this case,

\[ \mathcal{T}_{\text{ext}} = \frac{T_f (1 - R_u) e^{-\alpha x}}{1 - R_u R'_f e^{-2\alpha x}}, \]  
\[ \mathcal{R}_{\text{ext}} = \mathcal{R}_f + \frac{T_f^2 R_u e^{-2\alpha x}}{1 - R_u R'_f e^{-2\alpha x}}, \]  

where \( R_u \approx \frac{(n - 1)^2}{(n + 1)^2} \) is the reflectance of the quartz surface, \( \alpha \) is the absorption coefficient of the quartz, \( x \) is the thickness of the quartz substrate, and \( R'_f \) is the film reflection from inside the substrate,

\[ R'_f = \frac{(Z_0 \sigma_1 d - n + 1)^2 + (Z_0 \sigma_2 d)^2}{(Z_0 \sigma_1 d + n + 1)^2 + (Z_0 \sigma_2 d)^2}. \]  

Quartz has negligible absorption and dispersion over the spectral and temperature range of interest \([68]\). Thus we take \( \alpha = 0 \) and \( n = 2.12 \), yielding \( R_u \approx 0.13 \).

Our measurements give us the external transmission and reflection ratios, \( \mathcal{T}_{\text{ext,s}}/\mathcal{T}_{\text{ext,n}} \), and \( \mathcal{R}_{\text{ext,s}}/\mathcal{R}_{\text{ext,n}} \) that include the substrate. For range of conductivity values expected for the film, we find that, to a very good approximation, \( \mathcal{T}_{\text{ext,s}}/\mathcal{T}_{\text{ext,n}} = \mathcal{T}_s/\mathcal{T}_n \) and \( \mathcal{R}_{\text{ext,s}}/\mathcal{R}_{\text{ext,n}} = \mathcal{R}_s/\mathcal{R}_n \). Figure 4-3 compares the superconducting-state to normal-state transmittance and reflectance ratios, calculated using Eqs. (4–2) and (4–3), and Eqs. (4–6) and (4–7). The optical conductivity are taken to be that of NbTiN at 2 K, 0 T, calculated from the Mattis-Bardeen theory, shown in the left panel of Figure 4-4. The approximations \( \mathcal{T}_{\text{ext,s}}/\mathcal{T}_{\text{ext,n}} = \mathcal{T}_s/\mathcal{T}_n \) and \( \mathcal{R}_{\text{ext,s}}/\mathcal{R}_{\text{ext,n}} = \mathcal{R}_s/\mathcal{R}_n \) seem to work well, even though some small discrepancies exist at low frequency.

We measured \( \mathcal{T}_n \) and used it to calculate \( R_\square \) (Section 3.3.2), which in turn determines \( \mathcal{R}_n \). We use \( \mathcal{T}_n \) and \( \mathcal{R}_n \) to calculate \( \mathcal{T}_s \) and \( \mathcal{R}_s \) from our measured ratios. Then we invert Eqs. (4–2) and (4–3) to find

\[ \frac{\sigma_1}{\sigma_n} = \frac{n R_\square}{Z_0} \frac{1 - \mathcal{R}_s - \mathcal{T}_s}{\mathcal{T}_s}, \]  
\[ \frac{\sigma_2}{\sigma_n} = \frac{R_\square}{Z_0} \left[ \frac{4n}{\mathcal{T}_s} - (Z_0 \sigma_1 d + n + 1)^2 \right]^{1/2}. \]  

66
Figure 4-3. Left: comparison of $\frac{T_s}{T_n}$ and $\frac{T_{ext,s}}{T_{ext,n}}$. Right: comparison of $\frac{R_s}{R_n}$ and $\frac{R_{ext,s}}{R_{ext,n}}$. Material parameters are those of the NbTiN sample.

In the study of the NbN sample, since the transmission and reflection were measured at 30° angle of incidence, the equations are slightly different. The synchrotron radiation is predominantly vertically polarized as it enters the magnet. For the sample holders used to measure transmission and reflection in a parallel field, the polarization ends up parallel to the sample surface, i.e. p-polarized. The superconducting-state transmittance and reflectance in this polarization at an angle of incidence $\theta_i$ are derived in Appendix C, given by Eqs. (C–24) and (C–25),

$$T_s = \frac{4n \cos \theta_i}{(n + \cos \theta_i \cos \theta_i + Z_0 \sigma_1 d \cos \theta_i)^2 + (Z_0 \sigma_2 d \cos \theta_i)^2},$$  \hspace{1cm} (4–11)

$$R_s = \frac{(n - \cos \theta_i \cos \theta_i + Z_0 \sigma_1 d \cos \theta_i)^2 + (Z_0 \sigma_2 d \cos \theta_i)^2}{(n + \cos \theta_i \cos \theta_i + Z_0 \sigma_1 d \cos \theta_i)^2 + (Z_0 \sigma_2 d \cos \theta_i)^2},$$  \hspace{1cm} (4–12)

where $\theta_i$ is the angle of refraction. The corresponding normal-state transmittance and reflectance are

$$T_n = \frac{4n \cos \theta_i}{(n + \cos \theta_i \cos \theta_i + Z_0 \sigma_1 d \cos \theta_i)^2},$$  \hspace{1cm} (4–13)

$$R_n = \frac{(n - \cos \theta_i \cos \theta_i + Z_0 \sigma_1 d \cos \theta_i)^2}{(n + \cos \theta_i \cos \theta_i + Z_0 \sigma_1 d \cos \theta_i)^2},$$  \hspace{1cm} (4–14)
Figure 4-4. The optical conductivity of NbTiN and NbN in zero field at 3 K and 2 K, respectively, normalized to their normal-state conductivities. The solid lines are fits with the Mattis-Bardeen theory. The dashed lines are calculations with the theory.

which are used to calculate $T_s(30^\circ)$ and $R_s(30^\circ)$ from the measured $T_s(30^\circ)/T_n(30^\circ)$ and $R_s(30^\circ)/R_n(30^\circ)$. The optical conductivity can be inverted from Eqs. (4–11) and (4–12) directly without corrections for the angle of incidence,

$$\frac{\sigma_1}{\sigma_n} = \frac{n R_\square}{Z_0 \cos \theta_i} \frac{1 - T_s - R_s}{T_s},$$

$$\frac{\sigma_2}{\sigma_n} = \frac{R_\square}{Z_0 \cos \theta_i} \left[ \frac{4n \cos \theta_i}{T_s \cos \theta_i} - \left( \frac{Z_0}{R_\square} \frac{\sigma_1}{\sigma_n} \cos \theta_i + n + \frac{\cos \theta_i}{\cos \theta_i} \right)^2 \right]^{1/2}. \quad (4–15)$$

We made similar approximation that the effect from the MgO substrate can be neglected.

The optical conductivity at various fields normalized to the normal-state value $\sigma_n$ are shown in Figure 4-4, Figure 4-5, and Figure 4-6. $\sigma_2/\sigma_n$ has some data points missing because the terms under the square root in Eqs. (4–10) and (4–16) are not guaranteed to be positive for the measured transmission and reflection when noise is included.

4.4.2 Analysis of the Zero-Field Data

The temperature-dependent optical conductivity of dirty-limit type-II superconductors are well known from the Mattis-Bardeen theory, given by Eqs. (2–18) and (2–19) in Section 2.3.6. Using $\Delta$ as the only fitting parameter we fitted our zero-field $\sigma_1/\sigma_n$,
Figure 4-5. The real (circles) and imaginary (triangles) parts of the $T = 3$ K optical conductivity of NbTiN at different applied parallel magnetic fields, normalized to the normal-state conductivity. The solid lines are fits to $\sigma_1/\sigma_n$ using the pair-breaking theory. The dashed lines show the corresponding $\sigma_2/\sigma_n$ as determined by a Kramers-Kronig transform of the real part.
Figure 4-6. The real (circles) and imaginary (triangles) parts of the $T = 2$ K optical conductivity of NbN at different applied parallel magnetic fields, normalized to the normal-state conductivity. The solid lines are fits to $\sigma_1/\sigma_n$ using the pair-breaking theory. The dashed lines show the corresponding $\sigma_2/\sigma_n$ as determined by a Kramers-Kronig transform of the real part.
shown as the solid lines in Figure 4-4. The imaginary part $\sigma_2/\sigma_n$ was calculated from the Mattis-Bardeen theory using the fitted value of $\Delta$, shown as dashed lines. The fitted value of $\Delta$ is 12.8 cm$^{-1}$ for NbTiN and 17.9 cm$^{-1}$ for NbN. Since the temperature is much lower than $T_c$, we assume that $\Delta = \Delta_0$, the zero-field zero-temperature gap, which gives the values of $\Delta_0$ in Table 3-1. These values will be used in the analysis of the field-dependent data.

4.4.3 Analysis of the Field-Dependent Data

The solid lines in Figure 4-5 and Figure 4-6 are fits to the data using the pair-breaking theory as extended by Skalski et al. [106] to calculate $\sigma_1/\sigma_n$ at 0 K:

$$\frac{\sigma_1}{\sigma_n} = \frac{1}{\omega} \int_{-\Omega_G-\omega/2}^{\Omega_G+\omega/2} dq [n(q+\omega/2)n(q-\omega/2) + m(q+\omega/2)m(q-\omega/2)]$$

(4–17)

for $\omega \geq 2\Omega_G$ and zero otherwise, where

$$n(q) = \text{Re} \left( \frac{u}{u^2 - 1} \right),$$

(4–18)

$$m(q) = \text{Re} \left( \frac{1}{u^2 - 1} \right).$$

(4–19)

$u$ is the solution to

$$u\Delta = q + i\Gamma \frac{u}{\sqrt{u^2 - 1}},$$

(4–20)

with $\Delta$ the pair-correlation gap. This, in turn, can be determined from the pair-breaking parameter $\Gamma$ and the zero-field single-particle gap $\Delta_0$ using

$$\ln \left( \frac{\Delta}{\Delta_0} \right) = -\frac{\pi \Gamma}{4\Delta}$$

(4–21)

for $\Gamma < \Delta$. $\Omega_G$ in the integration limits is the effective spectroscopic gap,

$$\Omega_G = \Delta \left[ 1 - \left( \frac{\Gamma}{\Delta} \right)^{2/3} \right]^{3/2}$$

(4–22)

for $\Gamma < \Delta$. Using $\Delta_0$ determined from the $H = 0$ T results, we proceeded to fit $\sigma_1/\sigma_n$ for $H > 0$ T using only $\Gamma$ as an adjustable parameter. The imaginary part of the conductivity
Figure 4-7. Fit of the real-part optical conductivity in parallel field for NbTiN and NbN, taken from Figure 4-5 and Figure 4-6. The zero-field optical conductivities are from Figure 4-4.

(dashed lines in Figure 4-5 and Figure 4-6) was calculated by a Kramers-Kronig transform of the real part using Eq. (2–22). The temperature is low enough that the gap has reached its zero-temperature value. Thermal contribution to $\sigma_1$ is expected to be very small at low reduced temperature. The 0 K result Eq. (4–17) is expected to be valid for our data taken at $T/T_c \ll 1$.

Figure 4-7 shows the fitted $\sigma_1/\sigma_n$ at different fields. Clearly, the absorption edge moves to lower energy as the field increases. The field-induced change is more significant in NbN than in NbTiN.

4.4.4 Pair-Breaking Parameter

The quantity $\Gamma$ describes the strength of pair breaking and is determined by the mechanism of pair breaking. Typical mechanisms are paramagnetic impurities, exchange interactions, magnetic fields, and electric currents. In the case of magnetic-field-induced pair breaking, the specific mechanism of pair breaking depends on the sample geometry and the field orientation with respective to the sample [5].

In a thin film superconductor, for any perturbing Hamiltonian that breaks time-reversal symmetry, $\Gamma$ is proportional to the square of the perturbing Hamiltonian in the dirty limit
Table 4-1. Pair-breaking parameter, effective spectroscopic gap and pair-correlation gap of NbTiN (Column 2–4) and NbN (Column 5–7).

<table>
<thead>
<tr>
<th>$H$ (T)</th>
<th>$\Gamma$ (cm$^{-1}$/T$^2$)</th>
<th>$\Omega_G$ (cm$^{-1}$)</th>
<th>$\Delta$ (cm$^{-1}$)</th>
<th>$\Gamma$ (cm$^{-1}$/T$^2$)</th>
<th>$\Omega_G$ (cm$^{-1}$)</th>
<th>$\Delta$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>12.800</td>
<td>12.800</td>
<td>0.000</td>
<td>17.900</td>
<td>17.900</td>
</tr>
<tr>
<td>1</td>
<td>0.080</td>
<td>12.092</td>
<td>12.737</td>
<td>0.400</td>
<td>15.509</td>
<td>17.583</td>
</tr>
<tr>
<td>2</td>
<td>0.115</td>
<td>11.891</td>
<td>12.709</td>
<td>0.680</td>
<td>14.443</td>
<td>17.358</td>
</tr>
<tr>
<td>3</td>
<td>0.210</td>
<td>11.420</td>
<td>12.634</td>
<td>1.200</td>
<td>12.773</td>
<td>16.931</td>
</tr>
<tr>
<td>4</td>
<td>0.355</td>
<td>10.813</td>
<td>12.518</td>
<td>1.700</td>
<td>11.380</td>
<td>16.509</td>
</tr>
<tr>
<td>5</td>
<td>0.520</td>
<td>10.210</td>
<td>12.358</td>
<td>2.200</td>
<td>10.118</td>
<td>16.076</td>
</tr>
<tr>
<td>6</td>
<td>0.710</td>
<td>9.585</td>
<td>12.229</td>
<td>2.900</td>
<td>8.511</td>
<td>15.446</td>
</tr>
<tr>
<td>7</td>
<td>1.000</td>
<td>8.725</td>
<td>11.988</td>
<td>3.350</td>
<td>7.554</td>
<td>15.024</td>
</tr>
<tr>
<td>8</td>
<td>1.280</td>
<td>7.969</td>
<td>11.750</td>
<td>3.750</td>
<td>6.746</td>
<td>14.638</td>
</tr>
<tr>
<td>9</td>
<td>1.620</td>
<td>7.123</td>
<td>11.454</td>
<td>4.200</td>
<td>5.878</td>
<td>14.186</td>
</tr>
</tbody>
</table>

In the case where the perturbation is caused by a parallel magnetic field, and in the limit the sample is so thin that the order parameter can be treated as constant, $\Gamma$ is quadratic in field [3, 5],

$$\Gamma_\parallel = \frac{1}{6} \frac{De^2 d^2}{\hbar c^2} H^2,$$  \hspace{1cm} (4–23)

where

$$D = \frac{1}{3} \tau_{tr} v_f^2$$  \hspace{1cm} (4–24)

is the material diffusion constant. Here $\tau_{tr}$ is the transport collision time and $v_f$ is the Fermi velocity. When the magnetic field is perpendicular to the thin film, instead of breaking the time-reversal symmetry, it causes spatial variation of the order parameter which induces a finite pair-breaking parameter $\Gamma_v$. This pair-breaking parameter is linear in field,

$$\Gamma_v = \frac{1}{c} DeH.$$  \hspace{1cm} (4–25)

The pair-breaking parameters of NbTiN and NbN, as extracted from the data at different fields, are listed in Table 4-1 and plotted in Figure 4-8.

The pair-breaking parameter of NbTiN is quadratic in field, as expected for the case of a thin film in parallel field. A quadratic fit of the form given by Eq. (4–23) yields $De^2 d^2 / 6 \hbar c^2 = 0.020$ cm$^{-1}$/T$^2$. We estimate $\tau_{tr}$ from $\sigma_n = ne^2 \tau_{tr}/m$ and $R_\square = 1/\sigma_n d$, $\tau_{tr} =$
Figure 4-8. Field dependence of the pair-breaking parameter $\Gamma$, determined from the experimental optical conductivity (circles for NbTiN and squares for NbN). The solid line is a quadratic fit and the dashed line a linear fit.

$m/R\Box dne^2 \approx 1.89 \times 10^{-16}$ s, where $R\Box = 117 \Omega/\Box$, $d = 10$ nm and $n \approx 1.61 \times 10^{23}$ cm$^{-3}$ is the electron density of NbN [81] similar to that of NbTiN. If we take the Fermi velocity to be that of NbN [81], $v_f \approx 1.95 \times 10^8$ cm/s, then, $De^2d^2/6\hbar c^2 = 0.049$ cm$^{-1}$/T$^2$, consistent with the fitted value of 0.020 cm$^{-1}$/T$^2$ within the uncertainty of the materials parameters.

In contrast, the pair-breaking parameter of NbN is linear in field, consistent with Eq. (4–25). This suggests that the pair breaking is caused by the spatial variation of the order parameter. A linear fit of the form given by Eq. (4–25) to the field-dependent pair-breaking parameter of NbN yields $De/c = 0.464$ cm$^{-1}$/T. Using $R\Box = 48 \Omega/\Box$, $d = 70$ nm and $n \approx 1.61 \times 10^{23}$ cm$^{-3}$, we estimate $\tau_{tr} = m/R\Box dne^2 \approx 6.58 \times 10^{-17}$ s. Assuming again $v_f \approx 1.95 \times 10^8$ cm/s for NbN, we have $De/c = 0.671$ cm$^{-1}$/T, in agreement with the fitted value within the uncertainty of the materials parameters. This consistency supports that the pair-breaking mechanism is different in the NbN sample from that in the NbTiN sample. Even though the field is parallel to the NbN film surface, the film thickness is not thin enough to avoid the entering of vortices, making the pair breaking equivalent to that caused by a perpendicular magnetic field.
At this point, it should be pointed out that the optical conductivity given by Skalski et al. is valid for thin film superconductors with thickness so small that the order parameter can be assumed to be constant across the film. It is therefore not directly applicable to the case where spatial variation of the order parameter is present, as in the case of the NbN sample discussed above. However, Maki explicitly derived that in the high field region, such as in the gapless regime, for the case in which the electric field of the electromagnetic wave is parallel to the external static magnetic field, the optical conductivity has the same form as that given by Skalski et al. \[5, 108\]. Equivalence of the homogeneous and inhomogeneous situations is also pointed out by, e.g., Anthore et al. \[101\]. The analysis based on the optical conductivity given by Skalski et al. is therefore valid on this ground, but the order parameter is understood to be a spatially-averaged one, i.e., \[\sqrt{\langle|\Delta(r)|^2\rangle_{av}}\]. This also applies to both the pair-correlation gap and the effective spectroscopic gap of the NbN sample, to be discussed in the following section.

### 4.4.5 Pair-Correlation Gap and Effective Spectroscopic Gap

The shift of the excitation energy gap \(2\Omega_G\) due to the application of magnetic field has already been discussed, and can be seen from the absorption edge in \(\sigma_1/\sigma_n\). This gap \(\Omega_G\) and the pair-correlation gap \(\Delta\) are calculated using Eqs. (4–21) and (4–22). The results are listed in Table 4-1, and compared in Figure 4-9. Both \(\Omega_G\) and \(\Delta\) drop as field increases, but the reduction of \(\Omega_G\) is much greater at any given field. Both samples at the highest attainable field of 10 T are still far away from the gapless region where \(\Omega_G\) vanishes. The experimental and theoretical values of \(\Omega_G\) and the pair-correlation gap \(\Delta\) are in excellent agreement, as shown in Figure 4-9. The field dependence of the spectroscopic gap data of NbTiN is almost quadratic, while that of NbN is almost linear. A linear shift can be possibly due to paramagnetic effect, having the form \(\Omega_G = \Delta_0 - \mu_B H\) \[93\]. But this cannot be the case for the NbN sample, because if the field-dependent \(\Omega_G\) of NbN is fitted with a straight line, the slope is approximately \(-4.12 \text{ cm}^{-1}/\text{T}\), having a much greater magnitude than \(-\mu_B = -0.4659 \text{ cm}^{-1}/\text{T}\).
As mentioned in the previous section, the pair-correlation gap and the effective spectroscopic gap of NbN are spatially averaged values $\langle \Delta(r) \rangle_{av}$ and $\langle \Omega_G(r) \rangle_{av}$. The dimension of the field-induced spatial variation is on the order of the coherence length, which is much smaller than the wavelength of far-infrared radiation. The sample therefore behaves as a continuum, and the gaps are probed as spatially averaged ones.

### 4.4.6 Sum-Rule Analysis

The oscillator-strength sum rule

$$\int_0^{\infty} \sigma_1(\omega) d\omega = \frac{\pi ne^2}{2m},$$

(4–26)

where $n$ is the electron density and $e$ and $m$ are the charge and mass of the electron, requires the area under $\sigma_1(\omega)$ to be the same for normal and superconducting states. The ratio $\sigma_1/\sigma_n$ in Figure 4-7 is always less than unity; the missing spectral weight condenses to a $\delta$ function at zero frequency, which is a measure of pair condensate density and is directly related to the pair-correlation gap. Figure 4-7 therefore shows a weakening of superconductivity as the field increases. There is a limit in which the absorption edge
approaches 0, while the missing spectral weight remains finite. The superconductor enters a “gapless” region but still maintains superconducting properties.

Specifically, the missing spectral weight $A$ can be calculated using the sum rule,

$$A = \int_{0}^{\infty} \sigma_{n,1} d\omega - \int_{0}^{\infty} \sigma_1 d\omega = \int_{0}^{\infty} \sigma_{n,1} (1 - \frac{\sigma_1}{\sigma_{n,1}}) d\omega,$$

(4–27)

where $\sigma_{n,1} = \sigma_{n,0}/(1 + \omega^2 \tau^2)$ is the real part of the Drude conductivity in the normal state. Here $\sigma_{n,0}$ is the dc conductivity in the normal state, and $\tau$ is taken to be the previously-mentioned transport collision time, $\tau_{tr} \approx 1.89 \times 10^{-16}$ s for NbTiN and $\tau_{tr} \approx 6.58 \times 10^{-17}$ s for NbN. Note that when $\omega$ approaches $100\Omega_G$, $\sigma_1$ is already approximately equal to $\sigma_{n,1}$. Eq. (4–27) is calculated by changing the upper limit of the integral to $100\Omega_G$, and using Eq. (4–17) for $\sigma_1/\sigma_{n,1}$. We calculated the missing spectral weight $A$ at various fields for both samples. The results are compared with the pair-correlation gap $\Delta$ and effective spectroscopic gap $\Omega_G$ in Figure 4-9. We plot the square root of the missing spectral weight, which is proportional to the order parameter (recall that $A \propto n_s$ and $n_s \propto |\psi(r)|^2$). For both samples, the field dependence of $\sqrt{A}$ is very similar to that of the pair-correlation gap $\Delta$ rather than to the spectroscopic gap $\Omega_G$. This is consistent with the fact that it is the pair-correlation gap rather than the spectroscopic gap that characterizes the strength of superconductivity.

The $\delta$ function in $\sigma_1$ gives rise to a function of the form $A/\pi \omega$ that dominates the behavior of $\sigma_2$. The missing spectral weight $A$ can therefore be estimated from $\sigma_2$. In Section 2.3.6 we discussed the two terms in $\sigma_2$, expressed in Eq. (2–23). Notice that in the inset in the right panel of Figure 2-2, $\sigma_2$ can be approximated as $A/\pi \omega$ below the optical gap ($2\Delta_0/\hbar \omega > 1$), even though such an approximation could slightly overestimates the value of $A$ because of the steeper slope. Above the optical gap, $A/\pi \omega$ drops rapidly and becomes comparable to the term $\sigma_{2,>}$. For a more accurate analysis, one can calculate
Table 4-2. Superfluid density (in $10^{19}$ cm$^{-3}$) for NbTiN (Column 2–3) and NbN (Column 4–5). Column 2 and Column 4 are calculated using sum rule. Column 3 and Column 5 are calculated from $\sigma_2$. The average error of Column 2 is 0.85, and the average error of Column 5 is 0.48.

<table>
<thead>
<tr>
<th>$H$ (T)</th>
<th>$n_{SR,NbTiN}$</th>
<th>$n_{SL,NbTiN}$</th>
<th>$n_{SR,NbN}$</th>
<th>$n_{SL,NbN}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.69</td>
<td>6.06</td>
<td>1.82</td>
<td>1.77</td>
</tr>
<tr>
<td>1</td>
<td>3.66</td>
<td>5.77</td>
<td>1.74</td>
<td>1.73</td>
</tr>
<tr>
<td>2</td>
<td>3.65</td>
<td>5.62</td>
<td>1.70</td>
<td>1.65</td>
</tr>
<tr>
<td>3</td>
<td>3.63</td>
<td>5.67</td>
<td>1.64</td>
<td>1.66</td>
</tr>
<tr>
<td>4</td>
<td>3.57</td>
<td>5.57</td>
<td>1.57</td>
<td>1.52</td>
</tr>
<tr>
<td>5</td>
<td>3.51</td>
<td>5.46</td>
<td>1.51</td>
<td>1.52</td>
</tr>
<tr>
<td>6</td>
<td>3.44</td>
<td>5.35</td>
<td>1.42</td>
<td>1.37</td>
</tr>
<tr>
<td>7</td>
<td>3.33</td>
<td>5.26</td>
<td>1.35</td>
<td>1.41</td>
</tr>
<tr>
<td>8</td>
<td>3.25</td>
<td>5.17</td>
<td>1.30</td>
<td>1.26</td>
</tr>
<tr>
<td>9</td>
<td>3.14</td>
<td>4.95</td>
<td>1.24</td>
<td>1.29</td>
</tr>
<tr>
<td>10</td>
<td>2.95</td>
<td>4.83</td>
<td>1.16</td>
<td>1.21</td>
</tr>
</tbody>
</table>

$\sigma_{2,>} (\omega)$ from $\sigma_{1,>} (\omega)$, and subtract it from $\sigma_2 (\omega)$ to get $A/\pi \omega$. Using Eq. (2–22),

$$
\sigma_{2,>} (\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\sigma_{1,>} (\omega')}{\omega'^2 - \omega^2} d\omega'.
$$

(4–28)

The integral can be evaluated by splitting it into two parts. The first part is in the range between 0 and $100\Omega_G$, in which we use the pair-breaking optical conductivity for $\sigma_{1,>} (\omega)$, shown as solid lines in Figures 4-5 and 4-6. The second part is in the range above $100\Omega_G$, in which $\sigma_{1,>} (\omega)$ can be well approximated as $\sigma_{n,1} = \sigma_{n,0} / (1 + \omega^2 \tau^2)$. The total integral is subtracted from the $\sigma_2$ data, and compared with the original $\sigma_2$ data in Figure 4-10, plotted vs $1/\omega$. This difference between $\sigma_2$ and $\sigma_{2,>}$ is then fitted to the form $A/\pi \omega$ to extract the value of $A$, shown as solid lines in Figure 4-10. It works well for NbTiN, but for NbN a small y-intercept is needed to get a good linear fit. In Figure 4-11, the fitted value of $A$ are compared with those calculated using the sum rule. The two methods seem to give consistent field dependence, though the absolute value of $A$ differs, especially for NbTiN.

To get a sense of the order of magnitude of the superfluid density $n_s$, let us use the value of the missing spectral weight $A$ for an estimation. The linear fit of $\sigma_1/\sigma_n$ for
Figure 4-10. The imaginary part of the optical conductivity in parallel fields plotted vs $1/\omega$ for NbTiN (first column) and for NbN (second column). The triangles are the $\sigma_2/\sigma_n$ data. The circles are the difference between $\sigma_2/\sigma_n$ and $\sigma_2>/\sigma_n$. The solid lines are linear fits to the circles.
Figure 4-11. Field dependence of the missing spectral weight, normalized to its zero-field value. The triangles are results calculated from the sum rule, and the circles are estimated from the imaginary part of the optical conductivity $\sigma_2$. The error bars are from the linear fits in Figure 4-10.

NbTiN at 3 K, 0 T yields the value of the slope $A/\pi\sigma_n = n_se^2/2m\sigma_n = 33.02$ cm$^{-1}$. Convert to the unit of s$^{-1}$, $n_se^2/2m\sigma_n = 9.91 \times 10^{11}$ s$^{-1}$. The normal-state optical conductivity can be calculated from the sheet resistance $R_\parallel = 117$ $\Omega$ and the film thickness $d = 10$ nm, $\sigma_n = 1/R_\parallel d = 8.55 \times 10^3$ $\Omega^{-1}\cdot$cm$^{-1}$, in practical units. Converting to CGS units, $\sigma_n = 8.55 \times 10^3 \times 9 \times 10^{11}$ s$^{-1} = 7.70 \times 10^{15}$ s$^{-1}$. This determines $n_se^2/m = 1.53 \times 10^{28}$ s$^{-2}$. Converting to SI units, we have $n_se^2/4\pi\varepsilon_0 m = 1.53 \times 10^{28}$ s$^{-2}$. Therefore $n_s = 6.06 \times 10^{19}$ cm$^{-3}$. Similarly, for NbN at 2 K, 0 T, the linear fit in Figure 4-10 yields $n_se^2/2m\sigma_n = 27.86$ cm$^{-1}$. Using $\sigma_n = 2.98 \times 10^3$ $\Omega^{-1}\cdot$cm$^{-1}$, we estimated $n_s = 1.77 \times 10^{19}$ cm$^{-3}$. The values of superfluid density $n_{SR}$ calculated from the sum rule and the values of the superfluid density $n_{SI}$ calculated from $\sigma_2$ are listed in Table 4-2.

4.4.7 Comparison with Homes’s Law

With the estimated value of the superfluid density $n_s$, it is interesting to compare the data with Homes’s law. Homes et al. [109] discovered a simple scaling relation between the superfluid density and the product of $T_c$ and the d.c. conductivity just above $T_c$. If the superfluid density is converted to the associated spectral weight $A$, the relation can be
Figure 4-12. Comparison with Homes’s law. The circles are NbTiN data. The squares are NbN data. The solid line is Homes’s law for dirty-limit weak-coupling BCS superconductors. The dashed line is Homes’s law for cuprates.

written as

\[ A \simeq \alpha \sigma_{n,0} T_c, \]  

(4–29)

where \( A \) is in cm\(^{-2}\), \( \sigma_{n,0} \) and \( T_c \) are in cm\(^{-1}\) (1 cm\(^{-1}\)=\(\pi/15\) \(\Omega\cdot\) cm\(^{-1}\)=1.44 K). Within errors, the constant \( \alpha \) is approximately 4.4 for cuprate high-temperature superconductors, regardless of the doping, crystal structure and disorder type. The relation holds both in the a-b plain and along the c axis of cuprates. For BCS weak-coupling superconductors in the dirty limit, \( \alpha \) is about 8.1 [110]. These two scaling relations are shown as dashed line and straight line in Figure 4-12.

For our samples, the spectral weight associated with the superfluid at different fields is obtained in the previous section. We use the values calculated from the sum rule in the analysis here. The d.c. conductivity \( \sigma_{n,0} \) at 20 K are also estimated in the previous section, and it is independent of the magnetic field. The critical temperature \( T_c \) at different parallel fields is determined from the resistivity data shown in Figure 3-7.

Here we define \( T_c \) as the temperature at the middle of the transition in the resistance vs
Figure 4-13. Left: the pair-correlation gap $\Delta$, the critical temperature $T_c$, and the half effective spectroscopic gap $\Omega_G$ as a function of the pair-breaking parameter $\Gamma$. The dashed line is $\Delta^2$. All quantities are normalized to their zero-field values. Right: $\Delta^2$ vs $T_c$, compared to a straight line.

temperature plot. The spectral weight data $A$ are plotted vs $\sigma_{n,0}T_c$ in Figure 4-12, showing consistency with the scaling relation for dirty-limit weak-coupling BCS superconductors.

The linear relation between the spectral weight $A$ and the critical temperature $T_c$ can be verified directly from the pair-breaking theory. Noting the correlation between the square root of the missing spectral weight $\sqrt{A}$ and the pair-correlation gap $\Delta$ shown in Figure 4-9, we assume that $\sqrt{A} \propto \Delta$, or equivalently $A \propto \Delta^2$. The pair-correlation gap $\Delta(\Gamma)$ is solved from Eq. (4–21). The critical temperature as a function of the pair-breaking parameter is solved from the following equation [106],

$$\ln \left( \frac{T_c^P}{T_c} \right) = \psi \left( \rho + \frac{1}{2} \right) - \psi \left( \frac{1}{2} \right),$$

(4–30)

in which $\rho = \Gamma / 2\pi k_B T_c$, $T_c^P$ is the critical temperature at $\Gamma = 0$, and $\psi(x)$ is the digamma function,

$$\psi(x) = \frac{d}{dx} \ln \Gamma(x),$$

(4–31)

where $\Gamma(x)$ is the gamma function. The critical temperature $T_c$ as a function of the pair-breaking parameter is compared with the pair-correlation gap $\Delta$ and the effective
4.4.8 Density of States

It is instructive to compare the magnetic-field-modified quasiparticle density of states to the BCS density of states given by Eq. (2–14). The single-particle density of states given by the pair-breaking theory is

\[ N(\omega) = \text{Re} \left( \frac{u}{\sqrt{u^2 - 1}} \right) = n(q), \]  

where \( N(0) \) is the single-particle density of states at the Fermi level, and \( u \) is solved from Eq. (4–20). Using the fitted value of \( \Gamma \) of NbTiN at different fields, we calculated its density of states, shown in Figure 4-14. For each curve, there is an energy threshold above which quasiparticles can be created. This is exactly the spectroscopic gap, which shifts with field. The field-induced pair breaking also smears out the gap-edge singularity in the quasiparticle density of states [106], so that the initial rise of \( \sigma_1 \) becomes less abrupt for increasing fields. This slower increase is evident when comparing the results in Figure 4-7.
4.4.9 Consistency Check of the Fits

To check the consistency of the fits to the optical conductivity, we can use the fitted $\sigma_1/\sigma_n$ and $\sigma_2/\sigma_n$ to calculate the transmission or reflection, and then compare that with our raw data. The best quantity to compare is the transmission of NbTiN, because it is the only one measured at normal incidence. In this case the measurement is the most reliable, and the data do not involve complications due to the angle of incidence. $T_s/T_n$ is calculated from the fitted optical conductivity shown in Figure 4-5 using Eqs. (4–2), (4–3), (4–4), and (4–5). The result, shown in Figure 4-15, is in good agreement with the raw data, confirming the validity of the analysis.

4.5 Summary

In conclusion, we measured far-infrared transmission and reflection of two thin-film superconductors with different thickness in a magnetic field parallel to the film surface. The real and imaginary parts of the optical conductivity are derived from these data, the former showing the absorption edge suppressed due to the applied field. The optical conductivities can be fitted well by the pair-breaking theory, and the degree of gap suppresion is in good agreement with the theory. The coefficients in the field-dependent pair-breaking parameter $\Gamma$ are compared with those calculated from material parameters. The optical conductivities from the fit are used to calculate transmission, which is then compared with the raw transmission data. Both are consistent, demonstrating the validity of the analysis.

The field dependence of gap suppression is different in the two samples. The pair-breaking parameter $\Gamma$, which describes the degree of pair breaking and gap reduction, is almost quadratic in field for the thinner NbTiN sample, and is linear in field for the thicker NbN sample. This suggests different mechanisms of pair breaking in the two samples. The NbTiN film is thin enough to avoid the vortex regime even at the highest attainable field of 10 T. When a parallel magnetic field is applied, it breaks the time-reversal symmetry of the condensate paring and induces pair breaking with $\Gamma$.
quadartic in field. The NbN film is much thicker than the NbTiN so that even when the
applied field is parallel to the film surface, at the lowest field of 1 T vortices can exist
in the sample. This causes spatial variation of the order parameter, which induces pair
breaking with $\Gamma$ linear in field.
Figure 4-15. Superconducting-state to normal-state transmission ratio of NbTiN in parallel fields at $T = 3$ K. The circles are data. The solid lines are calculations using the fitted $\sigma_s/\sigma_n$ from the pair-breaking theory.
CHAPTER 5
MAGNETO-SPECTROSCOPY OF VORTEX STATE

5.1 Vortex State in Superconductors

Type-II superconductors in magnetic fields above the lower critical field $H_{c1}$ enter the vortex state. In the previous chapter, we have intentionally chosen the field orientation to be parallel to the thin film superconductors, so that such state might be avoided or at least vortex-induced effects can be minimized. In this chapter we apply the magnetic field perpendicular to the film surface to investigate the vortex-state electrodynamics of superconductors.

In the vortex state, magnetic fields partially penetrate superconductors in the form of quantized flux lines. Around the vortex cores, supercurrents circulate and screen the magnetic flux from the core interior; superconductivity persists in between the vortex cores. The properties of vortices and their interactions with the superconducting condensate have been studied since the discovery of conventional superconductors. An early model by Bardeen and Stephen [111] discussed the current-driven free vortex motion and its induced dissipation. Such motion is restrained by pinning forces due to spatial inhomogeneities in the superconductors. The crossover from the vortex-pinning regime to the flux-flow regime was first observed by Gittleman and Rosenblum [112, 113] in the microwave range for type-II superconductors. Interest in this field was revived by the discovery of high-temperature superconductors [114]. Flux-pinning and flux-creep contributions to the vortex dynamics were addressed, for example, by Coffey and Clem [115], Brandt [116], and Dulčić and Požek [117, 118]. In general, the applied field could modify the behaviors of both the condensate and the quasiparticles. While the modification of the quasiparticle states due to the vortices was observed in high-temperature superconductors [119], it was pointed out that vortex dynamics mainly affect the condensate in type-II superconductors [120].
5.2 Motivation

The understanding of the vortex state in type-II superconductors is meaningful in the sense that the mechanism of superconductivity is well known from BCS theory, which may simplify the problem. The properties of such a mixture of superconducting material and vortices can be probed by its electrodynamic response. With the established description of the Miessner-state electrodynamics of conventional superconductors by BCS Mattis-Bardeen theory [34], the vortex-induced change to the response functions should manifest itself in various observable quantities. Microwave techniques have been the prevailing tools in testing the theoretical models of vortex dynamics [121–126]. Due to the much lower energy scale of microwaves compared to the superconducting energy gaps, such techniques proved to be excellent for the detection of the condensate response. Infrared experiments, sensitive to the response of both the condensate and the quasiparticles, and capable of capturing the shifts of the spectral weight, are however scarce in literature for the study of vortex dynamics. Time-domain terahertz spectroscopy [127] and far-infrared transmission at a single frequency [128] were recently employed to study NbN thin films in the vortex state. Here we report frequency-dependent far-infrared transmission of NbTiN and NbN thin films penetrated by a static perpendicular magnetic field. The data are compared to the Maxwell-Garnett theory, the Bruggeman effective medium approximation, and the Coffey-Clem model. We demonstrate that for thin films it is necessary to consider the magnetic-field-induced pair breaking on the superconducting electrons outside of the vortex cores.

5.3 Experimental

The samples are the same NbTiN and NbN thin-film superconductors studied in the previous chapters. Their parameters are listed in Table 3-1. Far-infrared transmission and reflection measurements on these samples were performed at Beamline U4IR of the National Synchrotron Light Source, Brookhaven National Laboratory. The beamline is equipped with an IFS 66-v/S vacuum FT-IR spectrometer from Bruker Optics, modified
to use the synchrotron radiation as an external light source, and to include a $^4$He cryostat along with a superconducting magnet from Oxford Instrument for low-temperature magneto-spectroscopy. A composite silicon bolometer from Infrared Laboratories, operating at 1.6 K by pumping the helium coolant, detects the far-infrared radiation with high sensitivity. The system allows measurements to be performed in the spectral range of 10–110 cm$^{-1}$, the temperature range of 1.8–300 K, and the magnetic field range of 0–10 T. Both samples were measured in their superconducting state at 2 K, with the magnetic field applied perpendicular to the film surfaces and increased from 0 to 10 T. Normal-state transmission in zero field was measured at 20 K as a reference.

The samples were loaded at the bottom of a probe in the Faraday configuration shown in Figure 5-1 (external magnetic fields perpendicular to film surface). We started with transmission measurements. In the experiment layout shown in Figure 5-2, the plane mirror (A) for collecting the reflected light was taken out from the four-way cross-shaped flange, so that the incident beam (shown in red) can completely pass through. The transmitted signal (shown in green) is detected by the bolometer placed at Position P1, as shown in Figure 5-2. To apply the field perpendicular to the film, we first roughly loaded the samples in the approximate angle range, then carefully rotated the probe to maximize the transmission signal, as illustrated in Figure 5-1. The position was carefully marked for later reference. The error of the alignment is expected to be within 5°.
Figure 5-2. Optical layout for transmission and reflection measurements in a perpendicular magnetic field (this is a simplified version of the design made by G. Lawrence Carr). The red rays are the incident beam, the green rays the transmitted beam, and the blue rays the reflected beam. A plane mirror is installed in the four-way cross-shaped flange to direct beams in the reflection measurement, and is taken out to allow the full beam to pass in the transmission measurement. The bolometer is placed at Position P1 for transmission and moved to Position P2 for reflection measurement.
The reflection measurement was done immediately after the transmission measurement was finished. The sample was kept at the same position, with the orientation of the sample probe unchanged so that the magnetic field was perpendicular to the film surface. The plane mirror was installed to direct the reflected signal from the sample (shown in blue in Figure 5-2) to the bolometer, which was moved from Position P1 to Position P2 downstream of the plane mirror. The reflection measurement is complicated by the reflection from the quartz window on the magnet, which has a reflectance of about 23% (this is the calculated average reflectance for a quartz window of refractive index $n = 2.12$, including the effects from both surfaces), and therefore causes a significant amount of stray light. This stray light was measured by rotating the sample probe 45° from the marked position mentioned in the previous paragraph, and subtracted from all the single beam reflectance spectra of the samples. To minimize the stray light, the plane mirror (A) and the paraboloid (B) were manipulated to minimize the ratio of the stray signal and the signal from the sample at the marked position (true signal plus stray signal).

Both transmission and reflection were measured at a resolution of 4 cm$^{-1}$ to avoid interference fringes due to the multiple internal reflections of the incident waves in the substrate. The data at selected fields for both samples are shown in Figure 5-3. For both samples, when the magnetic field increases, the superconducting-state transmission approaches the normal-state transmission, suggesting the weakening of superconductivity. The peak position, as an indication of the optical gap frequency, does not show significant shift when the field increases. The two samples show essentially the same behavior in the $T_s/T_n$ and $R_s/R_n$ ratios. NbTiN has a much lower upper critical field than NbN so that at 10 T it is already close to the normal state.

5.4 Analysis

5.4.1 Extraction of Optical Conductivity

From the measured transmission and reflection, we can extract the optical conductivity using the same method employed in the previous chapter. The normal-state transmittance
Figure 5-3. Measured superconducting-state to normal-state ratios of transmission $\tau_s/\tau_n$ and reflection $R_s/R_n$ at various perpendicular magnetic fields. Stray light has been subtracted from the reflection single beam spectra before calculating the ratios.

is measured and the thin film normal-state sheet resistance $R_{\square}$ is calculated from Eq. (3–11). The value of the substrate refractive index $n$ is listed in Table 3-1. The normal-state reflectance is then calculated from Eq. (4–5). $\tau_n$ and $R_n$ are multiplied to the measured $\tau_s/\tau_n$ and $R_s/R_n$ to obtain the superconducting-state transmittance $\tau_s$ and reflectance $R_s$. The optical conductivity $\sigma$ is then extracted from them using Eqs. (4–9) and (4–10). The procedure in the configuration used here does not involve complications due to finite angle of incidence, because both transmission and reflection were measured at near normal incidence. The field-dependent optical conductivities are shown in Figure 5-4.
Figure 5-4. The optical conductivity of NbTiN and NbN extracted from transmission and reflection measured in perpendicular magnetic fields, normalized to their normal-state conductivities. The solid symbols are $\frac{\sigma_1}{\sigma_n}$, and the open symbols are $\frac{\sigma_2}{\sigma_n}$.

The extracted optical conductivity is a quantity characterizing the effective electrodynamic response of the vortex state. In the remaining part of this chapter we will use this quantity to test theories of vortex-state electrodynamics for type-II superconductors.

5.4.2 Analysis of Zero-Field Data

We begin our analysis with the zero-field optical conductivity. For our dirty-limit type-II superconducting samples, the Mattis-Bardeen theory provides explicit expressions for the real and imaginary parts of the optical conductivity, given by Eqs. (2–18) and (2–19). Assuming BCS temperature dependence of the gap $\Delta$ and using $\Delta_0$ as the only fitting parameter, we fitted the real part of the optical conductivity. The imaginary part was calculated from the Mattis-Bardeen theory using the fitted value of $\Delta_0$. The fit and calculation, shown in Figure 5-5, are in good agreement with the data. The value of the fitting parameter $\Delta_0$ agrees with those found in Section 4.4.2. The consistency of the zero-field optical conductivity for both samples obtained using the two different measurement configurations (as shown in the previous chapter and in this chapter) supports the reliability of both experimental methods.
Figure 5-5. The optical conductivity of NbTiN and NbN in zero field at 2 K, normalized to their normal-state conductivities. The solid lines are fits with the Mattis-Bardeen theory; the dashed lines are calculations with the theory.

5.4.3 Theories of Effective Optical Conductivity

To explain the magnetic-field dependence shown in Figure 5-4, we apply a few theories to study the effective optical response of the mixture of vortices and a superconducting material. The theories compared here are two effective medium theories and the Coffey-Clem model.

A basic assumption of the effective medium theories is that the grains are small compared to the wavelength of radiation, so that the inhomogeneous medium appears to be uniform to the external electromagnetic waves. Because the vortices, treated as grains embedded in a superconducting medium, are generally regarded as cylindrical tubes with radius of the coherence length (of the order of nanometers), and because the length of these cylindrical tubes are limited by the thin film thickness (less than 100 nm), this assumption can be satisfied in the far-infrared.

The two most widely-used approaches of the theories are the Maxwell-Garnett theory (MGT) and Bruggeman effective medium approximation (EMA) \([129, 130]\). The MGT approach treats the grains to be embedded in the surrounding medium. It is best suitable for the description of composites with the so-called “cermet topology” proposed by Lamb
et al. (left panel in Figure 5-6), in which inclusions are well separated [131]. In dilute mixtures such a topology can usually be achieved. The effective response functions vary smoothly with the volume fraction of the grains. Quite differently, the EMA approach treats all constituents in an equivalent way. This is valid in systems with the “aggregate topology” (right panel in Figure 5-6), in which all constituents are connected, making it ambiguous to define the host and the inclusion. Assuming the surrounding medium to be characterized by the effective properties of the inhomogeneous system, it is capable of describing mixtures with percolation occurring at certain mixture fractions. In our case, we expect the sample to be still partially superconducting even at high volume fraction of vortices, so that percolation does not occur. Moreover, the vortices correlate to stay apart because of the repulsive force between them. Hence, every vortex is surrounded by the superconducting fraction, which seems to be more consistent with the picture of cermet topology. We therefore expect MGT to be a better description of our case. Both theories are detailed below.

5.4.3.1 Maxwell-Garnett theory

Consider an inhomogeneous medium made of two components, grain $a$ with volume fraction $f$ embedded in the surrounding $b$ with volume fraction $1 - f$. The electromagnetic waves traversing the medium can be treated as a spatially-averaged field with its electric
component expressed as

\[ \langle \mathbf{E} \rangle = f \mathbf{E}_a + (1 - f) \mathbf{E}_b. \]  \hspace{1cm} (5-1)

The response function \( \mathbf{D} \) is similarly spatially averaged, expressed as

\[ \langle \mathbf{D} \rangle = f \epsilon_a \mathbf{E}_a + (1 - f) \epsilon_b \mathbf{E}_b. \]  \hspace{1cm} (5-2)

The effective dielectric function is defined as

\[ \epsilon_{\text{eff}} = \frac{\langle \mathbf{D} \rangle}{\langle \mathbf{E} \rangle}. \]  \hspace{1cm} (5-3)

The Maxwell-Garnet theory considers the electric field \( \mathbf{E}_a \) to be the local field acting on the grain \( a \). It consists of the external field and the field caused by the polarized charges on the surface of an artificial cavity in which the grain resides. In considering this local field, the theory assumes that the separation between grains are large enough so that individual grains scatter light independently. Further more, the field in the surrounding medium \( b \) is assumed to be unaffected by the presence of the grains \([132, 133]\). Based on these assumptions, the Maxwell-Garnett theory gives the effective dielectric function for oriented ellipsoid grains as

\[ \epsilon_{\text{MGT}} = \epsilon_b + \frac{f(\epsilon_a - \epsilon_b)}{g(1 - f)(\epsilon_a - \epsilon_b) + \epsilon_b}, \]  \hspace{1cm} (5-4)

where \( g \) is the depolarization factor determined by the shape of the ellipsoid. Using the relation \( \epsilon = 1 + 4\pi i\sigma/\omega \) (Appendix B), and writing \( \sigma_a = \sigma_n \) and \( \sigma_b = \sigma_s \), we have

\[ \frac{\sigma_{\text{MGT}}}{\sigma_n} = \frac{\sigma_s}{\sigma_n} + \left( \frac{\omega}{4\pi i\sigma_n} + \frac{\sigma_a}{\sigma_n} \right) \frac{f(1 - \frac{\sigma_s}{\sigma_n})}{g(1 - f)(1 - \frac{\sigma_s}{\sigma_n}) + \frac{\omega}{4\pi i\sigma_n} + \frac{\sigma_s}{\sigma_n}}. \]  \hspace{1cm} (5-5)

For our thin film samples, the term \( \omega/4\pi\sigma_n \) is much less than \( \sigma_2/\sigma_n \) in the frequency range \([10, 100]\) cm\(^{-1}\). For example, the NbTiN sample has \( R_\square = 117 \) \( \Omega/\square \) and film thickness \( d = 10 \) nm. Therefore in practical units \( \sigma_n^{\text{prac}} = 1/R_\square d = 8.55 \times 10^3 \) \( \Omega^{-1}\text{cm}^{-1} \). Converting to cgs units, \( \sigma_n^{\text{cgs}} = 7.69 \times 10^{14} \) s\(^{-1}\). The frequency range \([10, 100]\) cm\(^{-1}\) corresponds to
\[ \omega \in [3 \times 10^{11}, 3 \times 10^{12}] \text{s}^{-1}, \text{ so that } \omega/4\pi \varepsilon_0^\text{esu} \in [3.11 \times 10^{-5}, 3.11 \times 10^{-4}] \]. Therefore we can simplify the above equation to

\[
\frac{\sigma_{\text{MGT}}}{\sigma_n} = \frac{\sigma_s}{\sigma_n} + \frac{\sigma_s}{\sigma_n} \frac{f(1 - \sigma_s/\sigma_n)}{g(1 - f)(1 - \sigma_s/\sigma_n) + \sigma_s/\sigma_n}. \tag{5–6}
\]

This is equivalent to replacing all \( \varepsilon \)’s with \( \sigma \)'s in Eq. (5–4). Similar simplifications can be made for the NbN sample.

Vortices are generally regarded as cylindrical tubes with a normal core of radius of the coherence length \( \xi \), each carrying a quantum of magnetic flux \( \Phi_0 \) \[134\]. Outside of the core regions, the superconductor maintains superconducting properties. Setting \( g = 1/2 \) in the above equation for cylindrical grains, the effective optical conductivity is

\[
\frac{\sigma_{\text{MGT}}}{\sigma_n} = \frac{\sigma_s (1 + f)(1 - \sigma_s/\sigma_n) + 2\sigma_s/\sigma_n}{\sigma_n (1 - f)(1 - \sigma_s/\sigma_n) + 2\sigma_s/\sigma_n}, \tag{5–7}
\]

where \( f \) is the volume fraction of the vortices characterized by \( \sigma_n \).

### 5.4.3.2 Bruggeman effective medium approximation

Bruggeman proposed a method to address the issue that the grains and host material in Maxwell-Garnett theory are treated asymmetrically. Because of the presence of grains with different properties from the surrounding medium, the electric field in the region around the grains are modified, and the electric flux deviates from that when such grains are absent. Bruggeman argued that the average flux deviation for the whole medium should vanish \[132\]. He then suggested that an adequate choice of a self-consistent local field can satisfy this condition. This leads to the consideration of an effective medium in which all inclusions are treated on an equal basis, and the average flux deviation is zero \[133\]. Equivalently, the effective dielectric function can be calculated using Eqs. (5–1), (5–2), and (5–3). The difference from the Maxwell-Garnett theory is that there is no host medium in Bruggeman effective medium approximation. Both \( E_a \) and \( E_b \) are calculated assuming the constituents \( a \) and \( b \) are grains immersed in an effective medium characterized by an effective dielectric function.
For an inhomogeneous medium made of two components, grain $a$ of volume fraction $f$ embedded in the host material $b$ of volume fraction $1 - f$, Bruggeman effective medium approximation gives the effective dielectric function for oriented ellipsoid grains as the solution of the following equation,

$$f \frac{\epsilon_a - \epsilon_{EMA}}{g \epsilon_a + (1 - g) \epsilon_{EMA}} + (1 - f) \frac{b - \epsilon_{EMA}}{g \epsilon_b + (1 - g) \epsilon_{EMA}} = 0.$$ (5–8)

$\epsilon_{EMA}$ is one of the two solutions of this quadratic equation, with the imaginary part greater than or equal to zero. Since we treat the vortex as cylindrical particles, we set $g = 1/2$. The solution is

$$\epsilon_{EMA} = \frac{1}{2} \left[ (2f - 1)(\epsilon_a - \epsilon_b) + \sqrt{(2f - 1)^2(\epsilon_a - \epsilon_b)^2 + 4\epsilon_a \epsilon_b} \right].$$ (5–9)

Only this one out of the two solutions of the quadratic equation (5–8) is chosen, because it reduces to the correct values in the limit $f \to 0$ and $f \to 1$. Using the relation $\epsilon = 1 + 4\pi i \sigma/\omega$, and writing $\sigma_a = \sigma_n$ and $\sigma_b = \sigma_s$, we have the effective optical conductivity

$$\frac{\sigma_{EMA}}{\sigma_n} + \frac{\omega}{i4\pi \sigma_n} = \frac{1}{2} \left[ (2f - 1)(1 - \frac{\sigma_s}{\sigma_n}) + \sqrt{(2f - 1)^2(1 - \frac{\sigma_s}{\sigma_n})^2 + 4(\frac{\sigma_s}{\sigma_n} + \frac{\omega}{i4\pi \sigma_n})} \right].$$ (5–10)

Since $\omega/4\pi \sigma_n \in [3.11 \times 10^{-5}, 3.11 \times 10^{-4}]$ for NbTiN and similarly negligible for NbN, the above equation can be simplified as

$$\frac{\sigma_{EMA}}{\sigma_n} = \frac{1}{2} \left[ (2f - 1)(1 - \frac{\sigma_s}{\sigma_n}) + \sqrt{(2f - 1)^2(1 - \frac{\sigma_s}{\sigma_n})^2 + 4\frac{\sigma_s}{\sigma_n}} \right].$$ (5–11)

## 5.4.3.3 Coffey-Clem model

The effective medium theories discussed above treat vorticies as static grains embedded in a superconducting surrounding. Coffey and Clem [115, 135] proposed a theory to calculate the rf (radio-frequency) surface impedance of type-II superconductors under the influence of vortex dynamics. The theory generalized the two-fluid model.
to self-consistently couple the supercurrent density with the vortex displacements. It considers the Lorentz force exerted on the vortices due to the two-fluid current density 

\[ \mathbf{J} = \mathbf{J}_n + \mathbf{J}_s, \]

where \( \mathbf{J}_n \) and \( \mathbf{J}_s \) are the normal-fluid current density and supercurrent density, respectively. This force redistributes the vortices, induces ac currents due to the change of the vortex-induced fields, and results in the change of the total current density \( \mathbf{J} \). The central result is the frequency, field, and temperature dependent complex penetration depth \( \tilde{\lambda}(\omega, H, T) \). For the case of a thin film on a substrate in a perpendicular field \( H \), and for normally-incident rf waves with frequency \( \omega \) [135],

\[ \tilde{\lambda}(\omega, H, T) = \left[ \frac{\lambda^2(H, T) + (i/2)\tilde{\delta}_{vc}^2(\omega, H, T)}{1 - 2i\lambda^2(H, T)/\tilde{\delta}_{nf}^2(\omega, H, T)} \right]^{1/2}, \quad (5–12) \]

where \( \lambda(H, T) \) is the penetration depth associated with the supercurrent, \( \tilde{\delta}_{vc} \) is the complex effective skin depth due to vortex motion and flux creep, and \( \delta_{nf} \) is the normal-fluid skin depth. \( \lambda(H, T) \) is related to the zero-field penetration depth \( \lambda(0, T) \) through

\[ \lambda(H, T) = \lambda(0, T)/(1 - b)^{1/2}, \]

where \( b = H/H_{c2}^\perp \) is the reduced field with respect to the perpendicular upper critical field \( H_{c2}^\perp \), which we take as the vortex volume fraction \( f \).

\[ \tilde{\delta}_{vc} = \left( 2\tilde{\rho}_v/\mu_0\omega \right)^{1/2} \]

where \( \tilde{\rho}_v \) is the complex effective resistivity associated with the local vortex-motion-induced electric field,

\[ \frac{\tilde{\rho}_v(\omega)}{\rho_f} = \frac{\epsilon + (\omega \tau)^2 + i(1 - \epsilon)\omega \tau}{1 + (\omega \tau)^2}, \quad (5–13) \]

in which \( \rho_f = \rho_n f = f/\sigma_n \) is the flux flow resistivity, \( \epsilon \) is the flux-creep factor, and \( \tau \) is the characteristic relaxation time of the vortex motion. The field and temperature dependence of the normal-fluid skin depth takes the form

\[ \delta_{nf}^2 = \frac{\delta_n^2}{[1 - (1 - t^4)(1 - b)]}, \]

where \( \delta_n = \left( 2\rho_n/\mu_0\omega \right)^{1/2} \) is the normal-state skin depth, and \( t = T/T_c \) is the reduced temperature. Note the relation between the complex penetration depth and the complex optical conductivity \( \sigma_{CC} \equiv \tilde{\sigma} = i/\mu_0\omega\tilde{\lambda}^2 \), and assume a similar relation between the zero-field penetration depth \( \lambda(0, T) \) and the superconducting optical conductivity \( \sigma_s \),

\[ \sigma_s = i/\mu_0\omega\lambda^2(0, T), \]

we obtain the complex optical conductivity in the low temperature
limit \( t \ll 1 \),
\[
\frac{\sigma_{CC}}{\sigma_n} \approx \frac{(1-f)\sigma_s/\sigma_n + f}{\beta f(1-f)\sigma_s/\sigma_n + 1}.
\] (5–14)

\( \beta \) is defined as
\[
\beta \equiv \frac{\tilde{\rho}_n}{\rho_f} \approx \frac{1}{1 - i\omega_0/\omega},
\] (5–15)

where \( \omega_0 = 1/\tau \) is the characteristic frequency that distinguishes the flux-pinning and flux-flow regimes, called depinning frequency. Eq. (5–14) reduces to correct values in the limits \( f \to 0 \) and \( f \to 1 \). In Eq. (5–15) the effect of thermal creep has been neglected in the low temperature limit by setting \( \epsilon \to 0 \).

5.4.3.4 Comparison of theories

The theories discussed above are compared in Figure 5-7. The effective optical conductivities are calculated using Eqs. (5–7), (5–11), and (5–14) with various values of the normal-volume fraction \( f \). \( \sigma_s/\sigma_n \) is taken to be that of NbTiN at 0 T, shown in Figure 5-5. In Eq. (5–14) of the Coffey-Clem model the depinning frequency \( \omega_0 \) is set to 300 cm\(^{-1} \), assuming the flux-pinning regime.

The optical conductivities calculated from the three theories show very similar behavior above the gap, but are distinctive below the gap. The most significant difference is in the real part of \( \sigma_{eff}/\sigma_n \). \( \text{Re}(\sigma_{eff}/\sigma_n) \) calculated from both the Maxwell-Garnett theory and the Coffey-Clem model approaches a constant level as the frequency is lowered to zero. In contrast, \( \text{Re}(\sigma_{eff}/\sigma_n) \) calculated from Bruggeman effective medium approximation tends to increase with decreasing frequency below the gap. The asymptotic behavior of \( \text{Re}(\sigma_{eff}/\sigma_n) \) as the frequency approaches zero distinguishes the Bruggeman effective medium approximation from the other two theories.

The Maxwell-Garnett theory can be distinguished from the Coffey-Clem model by noticing two features. As the frequency is lowered from above to below the gap, there is a minimum in the \( \text{Re}(\sigma_{eff}/\sigma_n) \) calculated from the Maxwell-Garnett theory, but the one calculated from the Coffey-Clem model simply becomes a constant. Furthermore, as the normal-volume fraction \( f \) increases, the near-zero-frequency constant level in \( \text{Re}(\sigma_{eff}/\sigma_n) \)
Figure 5-7. The effective optical conductivity calculated from the Maxwell-Garnett theory (MGT), the Bruggeman effective medium approximation (EMA), and the Coffey-Clem model. $f$ is the normal-volume fraction.

approaches one much faster in Maxwell-Garnett theory than in the Coffey-Clem model. For example, in the last sub-plot in Figure 5-7, the constant level is almost at one for the Maxwell-Garnett theory, but it is at around 0.8 for the Coffey-Clem model. In fact, one can derive from Eqs. (5–7) and (5–14) that as frequency approaches zero, 

\[ \text{Re}(\sigma_{\text{MGT}}/\sigma_n) \to \frac{4f}{(1 + f)^2} \] 

in the Maxwell-Garnett theory, and 

\[ \text{Re}(\sigma_{\text{CC}}/\sigma_n) \to f \] 

in the Coffey-Clem model. This is again under the assumption of the flux-pinning regime, where the depinning frequency $\omega_0$ is much greater than the upper limit of our spectrum. Note
that the limiting constant level obtained from the Coffey-Clem model is independent of the depinning frequency $\omega_0$ in the flux-pinning regime.

When we compare these features in the theories to those in our data shown in Figure 5-4, we conclude that the Maxwell-Garnett theory is the closest interpretation of our data among the three. The reasons are the following. Firstly, the $\text{Re}(\sigma_{\text{eff}}/\sigma_n)$ data never exceed one for both samples. This rules out the Bruggeman effective medium approximation. Secondly, as the frequency is lowered from above to below the gap, a minimum feature is apparent in the $\text{Re}(\sigma_{\text{eff}}/\sigma_n)$ data in both samples. This is not accounted for by the Coffey-Clem model, but is consistent with the Maxwell-Garnett theory.

In the remaining part of this chapter, we will focus on the Maxwell-Garnett theory and use it to analyze the field-dependent optical conductivity shown in Figure 5-4.

### 5.4.4 Analysis of the Field-Dependent Data

We used the effective optical conductivity given by Eq. (5–7) to fit the data shown in Figure 5-4. The effective optical conductivity, expressed as

$$\frac{\sigma_{\text{MGT}}}{\sigma_n} = \frac{\sigma_s (1 + f)(1 - \sigma_s/\sigma_n) + 2\sigma_s/\sigma_n}{\sigma_n (1 - f)(1 - \sigma_s/\sigma_n) + 2\sigma_s/\sigma_n},$$

(5-4)

has two variables. $\sigma_s/\sigma_n$, the optical conductivity of the superconducting fraction, is assumed to be the same as the zero-field optical conductivity [3] shown in Figure 5-5. For convenience we used the fitted results in Figure 5-5 in the analysis presented here. The normal-volume fraction $f$ is the only fitting parameter that is varied to fit the real part of the optical conductivity at different fields. All fits were eye-balled. Once an optimal value of $f$ was found at a given field, it was used to calculate the imaginary part of the optical conductivity using Eq. (5–7). The results are shown in Figure 5-8 and Figure 5-9 for NbTiN and NbN, respectively.

For both samples, the fits are quantitatively consistent with the data. The dip feature located around the gap frequency in the real part of the optical conductivity is well
Figure 5-8. The real (circles) and imaginary (triangles) parts of the $T = 2$ K optical conductivity of NbTiN at different applied perpendicular magnetic fields, normalized to the normal-state conductivity. The solid lines are fits to $\sigma_1/\sigma_n$ using the Maxwell-Garnett theory. The dashed lines show the corresponding $\sigma_2/\sigma_n$ as calculated from the same theory.
Figure 5-9. The real (circles) and imaginary (triangles) parts of the $T = 2$ K optical conductivity of NbN at different applied perpendicular magnetic fields, normalized to the normal-state conductivity. The solid lines are fits to $\sigma_1/\sigma_n$ using the Maxwell-Garnett theory. The dashed lines show the corresponding $\sigma_2/\sigma_n$ as calculated from the same theory.
captured by the fits. However, for both samples, the dip appears at a lower frequency in the data than in the fits, especially for NbN. Moreover, for NbN the dip seems shallower in the data than in the fits. According to the oscillator-strength sum rule expressed by Eq. (2–20), these two facts point to the evidence that the extracted real part of the optical conductivity has less missing area compared to that in the fitted optical conductivity, indicating weaker superconductivity. Another evidence to support this point of view is from the below-gap behavior of the imaginary part of the optical conductivity, which takes the form $A/\omega$ with the constant $A$ proportional to the condensate density. The imaginary part of the optical conductivity data, especially that of NbN, deviate from the fit as the field increases, indicating more weakening of superconductivity than in the fits. Therefore, one might argue that using the zero-field $\sigma_s/\sigma_n$ is not adequate, and additional weakening of superconductivity is present. This will be discussed in the following section.

5.4.5 Pair-Breaking Effects

In the analysis we have presented so far, we made a widely-used assumption that the superconducting state outside of the vortex cores is unaffected by the external magnetic field. While this may be valid for bulk samples, it could be inadequate for thin films through which magnetic fields can easily penetrate. Magnetic fields have been proven to break the time-reversal symmetry of the Cooper pairs in both type-I and type-II thin superconducting samples, inducing pair-breaking effects [136, 137]. Such effects smear out the singularity in the quasiparticle density of states and modifies the optical conductivity $\sigma_s$. One manifestation of such field-induced modification is the suppression of the optical gap revealed in the real part of $\sigma_s$, which has been demonstrated in our study of the NbTiN and NbN thin films placed in parallel magnetic fields, discussed in Chapter 4. This motivates us to re-evaluate our analysis based on the Maxwell-Garnett theory, using the pair-breaking optical conductivity for $\sigma_s$ in Eq. (5–7) instead of the unperturbed one at zero field.
The NbN sample is a better example to test the influence of the pair-breaking effects than the NbTiN sample for two reasons. Firstly, the weakening of superconductivity due to vortices needs to be small enough so that the pair-breaking effects can play some noticeable role. We have estimated in Section 3.3.4 that at 2 K, $H_{c2}^{\perp}$ of the NbN sample is about 49.55 T, and $H_{c2}^{\perp}$ of the NbTiN sample is about 12.50 T. In the field range of 0–10 T, the amount of vortices can be small in the NbN sample, but is significant in the NbTiN. This is evident in the field-dependent transmission and reflection data shown in Figure 5-3: $T_s/T_n$ and $R_s/R_n$ for NbTiN quickly approaches one as the field is increased to 10 T, but they still show robust superconducting features at 10 T for NbN. Secondly, to include the effects of pair breaking in the analysis, it is important to identify the mechanism of pair breaking and to correctly calculate the pair-breaking optical conductivity. Because the transmission and reflection measurements presented in this chapter were done in perpendicular fields, we expect pair breaking induced by the spatial variation of the order parameter. In the previous chapter, we have found such effects in the NbN sample. We may use those results to analyze the data in this chapter. For the NbTiN sample, we observed a different type of pair-breaking induced directly by time-reversal symmetry breaking. The corresponding optical conductivity cannot be applied to the analysis here.

Using the normalized pair-breaking optical conductivity shown in Figure 4-6 as the $\sigma_s/\sigma_n$ in Eq. (5-7), and using the value of $f$ yielding the fits of the NbN data in Figure 5-9, we calculated the effective optical conductivity from Eq. (5-7). The results are shown in Figure 5-10 as solid lines. The dashed lines are the effective optical conductivity calculated using the zero-field optical conductivity, taken directly from Figure 5-9 for comparison.

The inclusion of the pair-breaking effects significantly improves the quality of the fits, especially at high fields where the pair-breaking effects are the most significant. The dip in the calculated optical conductivity matches well with that in the data. Moreover, the
Figure 5-10. The real (circles) and imaginary (triangles) parts of the $T = 2\,\text{K}$ optical conductivity of NbN at different applied perpendicular magnetic fields, normalized to the normal-state conductivity. The solid lines are fits using the Maxwell-Garnett theory with the inclusion of pair-breaking effects. The dashed lines are fits without the pair-breaking effects, taken directly from Figure 5-9.
below-gap part of the calculated $\text{Im}(\sigma_{\text{MGT}}/\sigma_n)$ describes the behavior of the data very well. The improvement of the fits supports the argument that it is necessary to consider the pair-breaking effects on the superconducting fraction of the vortex state when the effective electrodynamic response of the thin film superconductor is calculated.

5.4.6 Consistency Check of the Fits

As what we did in the previous chapter to check the quality of the fits to the optical conductivity data, we can similarly use the fitted optical conductivity we obtained above to calculate the transmission ratio, then compare with the raw data. Transmission is picked because it is easier to measure than reflection, thus more reliable. We use the fitted effective optical conductivity shown in Figure 5-9 and Figure 5-10 to calculate the transmission ratio according to Eqs. (4–2) and (4–4). The results are shown in Figure 5-11. Inclusion of the pair-breaking effects clearly makes the fits consistent with the data, confirming the conclusion reached at the end of Section 5.4.5.

5.4.7 Fitting Parameters

The analysis presented above yields the values of the fitting parameter, the normal-volume fraction $f$. Its value at different fields for both samples are listed in Table 5-1 and shown in Figure 5-12. It is typically assumed that $f = H/H_{c2}^\perp$. A linear fit of the $f$ vs $H$ data to the form $f = aH$ yields an estimate of $H_{c2}^\perp$. Such fits to the $f$ obtained from both samples are shown as straight lines in Figure 5-12. The fitted value for the slope is 0.092 T$^{-1}$ for NbTiN and 0.039 T$^{-1}$ for NbN. These correspond to an upper critical field of 10.87 T for NbTiN and 25.64 T for NbN. For NbTiN, the estimated value is consistent with the value listed in Table 3-1. For NbN, however, the $H_{c2}^\perp$ extrapolated to 2 K from the four-probe resistivity measurement may not be accurate. Therefore it is difficult to make a reliable comparison. The field dependence of the normal-volume fraction $f$ of NbN can be fitted better with a square-root form $f = a\sqrt{H}$ with $a = 0.11$ T$^{-1/2}$, though such a form is unexpected.
Figure 5-11. Superconducting-state to normal-state transmission ratio data of NbN in perpendicular fields (circles). The solid lines are calculations taking into account the pair-breaking effects, while the dashed lines do not include such effects.
Table 5-1. Normal-volume fraction $f$ for NbTiN and NbN.

<table>
<thead>
<tr>
<th>$H$ (T)</th>
<th>$f$ of NbTiN</th>
<th>$f$ of NbN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>0.140</td>
<td>0.090</td>
</tr>
<tr>
<td>2</td>
<td>0.240</td>
<td>0.150</td>
</tr>
<tr>
<td>3</td>
<td>0.330</td>
<td>0.180</td>
</tr>
<tr>
<td>4</td>
<td>0.400</td>
<td>0.220</td>
</tr>
<tr>
<td>5</td>
<td>0.480</td>
<td>0.240</td>
</tr>
<tr>
<td>6</td>
<td>0.560</td>
<td>0.260</td>
</tr>
<tr>
<td>7</td>
<td>0.640</td>
<td>0.285</td>
</tr>
<tr>
<td>8</td>
<td>0.710</td>
<td>0.300</td>
</tr>
<tr>
<td>9</td>
<td>0.800</td>
<td>0.315</td>
</tr>
<tr>
<td>10</td>
<td>0.890</td>
<td>0.320</td>
</tr>
</tbody>
</table>

Figure 5-12. Field dependence of the normal-volume fraction for NbTiN and NbN. The solid and dashed lines are fits to the form $f = aH$, yielding $a = 0.092 \text{T}^{-1}$ for NbTiN and $a = 0.039 \text{T}^{-1}$ for NbN. The dash-dotted line is fit to the $f$ of NbN to the form $f = a\sqrt{H}$, yielding $a = 0.11 \text{T}^{-1/2}$.

5.4.8 Superfluid Density

To learn how much the magnetic field is weakening the superconducting state, we can also estimate the superfluid density from the imaginary part of the optical conductivity. The method of estimation is the same as that used in Section 4.4.6.
Table 5-2. Superfluid density (in $10^{19}$ cm$^{-3}$) for NbTiN (Column 2) and NbN (Column 3), calculated from $\sigma_2$. The average error of Column 2 is 0.24, and the average error of Column 3 is 0.01.

<table>
<thead>
<tr>
<th>$H$ (T)</th>
<th>$n_{s,NbTiN}$</th>
<th>$n_{s,NbN}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.29</td>
<td>1.79</td>
</tr>
<tr>
<td>1</td>
<td>4.97</td>
<td>1.29</td>
</tr>
<tr>
<td>2</td>
<td>3.99</td>
<td>1.12</td>
</tr>
<tr>
<td>3</td>
<td>3.36</td>
<td>0.98</td>
</tr>
<tr>
<td>4</td>
<td>2.67</td>
<td>0.86</td>
</tr>
<tr>
<td>5</td>
<td>2.38</td>
<td>0.83</td>
</tr>
<tr>
<td>6</td>
<td>2.04</td>
<td>0.81</td>
</tr>
<tr>
<td>7</td>
<td>1.91</td>
<td>0.76</td>
</tr>
<tr>
<td>8</td>
<td>1.55</td>
<td>0.70</td>
</tr>
<tr>
<td>9</td>
<td>1.01</td>
<td>0.69</td>
</tr>
<tr>
<td>10</td>
<td>0.20</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Firstly, we calculate $\sigma_{2,>} (\omega)$ from $\sigma_{1,>} (\omega)$,

$$\sigma_{2,>} (\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\sigma_{1,>} (\omega')}{\omega'^2 - \omega^2} d\omega'. \tag{5-16}$$

The integral can be evaluated by splitting it into two parts. The first part is in the range between 0 and 100$\Omega_G$, in which we use the effective optical conductivity for $\sigma_{1,>} (\omega)$, shown as solid lines in Figures 5-8 and 5-10. The second part is in the range above 100$\Omega_G$, in which $\sigma_{1,>} (\omega)$ can be well approximated as $\sigma_{n,1} = \sigma_{n,0} / (1 + \omega^2\tau^2)$.

Secondly, the integral Eq. (5-16) is subtracted from the $\sigma_2$ data, and compared with the original $\sigma_2$ data in Figure 5-13, plotted vs $1/\omega$. This difference between $\sigma_2$ and $\sigma_{2,>}$ is then fitted to the form $A/\pi\omega$ to extract the value of $A$. The fits are shown as solid lines in Figure 5-13. It works well for NbTiN, but for NbN a small y-intercept is needed to get a good linear fit. The value of $A$ is then converted to the superfluid density $n_s$ using the relation $A = \pi n_s e^2 / 2m$. The results are listed in Table 5-2, and plotted in Figure 5-14. As the field increases, the superfluid density in NbTiN drops more drastically than in NbN because the upper critical field is much lower in the former. At 10 T, NbTiN almost has no superfluid left, while NbN still has almost 40% of superfluid as compared to 0 T.
Figure 5-13. The imaginary part of the optical conductivity in perpendicular fields plotted vs $1/\omega$ for NbTiN (first column) and for NbN (second column). The triangles are the $\sigma_2/\sigma_n$ data. The circles are the difference between $\sigma_2/\sigma_n$ and $\sigma_{2,>}/\sigma_n$. The solid lines are linear fits to the circles.
Figure 5-14. Field dependence of the superfluid density $n_s$ normalized to its zero-field value, estimated from the imaginary part of the optical conductivity $\sigma_2$. The error bars are from the linear fits in Figure 5-13.

5.4.9 Discussions of Flux-Pinning and Flux-Flow Regimes

We focused on the Maxwell-Garnett theory and used it to fit our optical conductivity data. In doing so we have implicitly assumed that the vortices are stationary, because the Maxwell-Garnett theory does not take into account possible dynamics of the grains. It is therefore important to know if our samples are in the flux-pinning regime under the experiment conditions.

A similar infrared spectroscopic study of a 80-nm-thick NbN film [128] assumed their sample to be in the flux-pinning regime. But the depinning frequency reported on some other conventional superconductors by microwave measurements are smaller than the lower limit of our spectrum. For example, Sarti et al. [123] determined the upper limit of $\omega_0$ for a 100-nm-thick MgB$_2$ film to be 0.33 cm$^{-1}$. Janjušević et al.[124] found that decreasing the thickness of their Nb thin films from 160 nm to 10 nm increases $\omega_0$ from 0.03 cm$^{-1}$ to 0.66 cm$^{-1}$. They suggested that for thin films placed in a perpendicular magnetic field, vortex pinning could be dominated by surface pinning centers, which may cause the pinning of vortices. This may happen in our samples.
We estimate the depinning frequency $\omega_0$ for our thin film samples, using an expression given by Gittleman and Rosenblum [113],

$$\omega_0 = \frac{2\pi c J_c}{\sigma_n H_{c2} \sqrt{\Phi_0}},$$  \hspace{1cm} (5–17)

where $J_c$ is the critical current, $\Phi_0$ is the magnetic flux quantum, and $H_{c2}$ is the upper critical field. The relation between the thermodynamic critical field $H_c$ and the parallel upper critical field $H_{c2}^\parallel$ for a superconducting thin film is given by Eq. (2–48) as $H_{c2}^\parallel = 2\sqrt{6} H_c \lambda/d$, where $\lambda$ is the penetration depth and $d$ is the film thickness. Four-probe resistivity measurements of the NbTiN thin film in parallel fields up to 16 T estimated $H_{c2}^\parallel$ at 2 K to be 22.0 T. NbTiN typically has a penetration depth $\lambda \approx 300$ nm (Table 3-1). Since $d = 10$ nm, we have $H_c \approx 0.15$ T. This, according to formula of the critical current of a thin film superconductor by Eq. (2–46) $J_c = cH_c/3\sqrt{6}\pi\lambda$, gives $J_c \approx 21.62$ MA/cm$^2$. Noting that $\sigma_n = 1/R_{\square}d = 8.55 \times 10^3$ $\Omega^{-1}$ cm$^{-1}$, and $H_{c2} \approx 11.2$ T in perpendicular fields, from Eq. (5–17) we have $\omega_0$ ranging from 16.5 cm$^{-1}$ to 52.2 cm$^{-1}$ between 1 T and 10 T. Using the material parameters of the NbN sample, the calculated $\omega_0$ ranges from 109.3 cm$^{-1}$ to 345.6 cm$^{-1}$ between 1 T and 10 T. It is therefore possible that the NbTiN sample is in the flux-flow regime, and the NbN in flux-pinning regime.

To see if taking into account flux flow can improve the Coffey-Clem theory as a model to explain our data, we calculated the effective optical conductivity $\sigma_{CC}/\sigma_n$ from Eq. (5–14) using different values of the depinning frequency $\omega_0$. The results are shown in Figure 5-15. As the depinning frequency is decreased below the upper limit of our spectrum, the optical conductivity behaves very differently. The above-gap part of the Re($\sigma_{CC}/\sigma_n$) is reduced by a great amount, making it smaller than observed in the data shown in Figure 5-4. Far into the flux-flow regime, e.g., the case $\omega_0 = 3$ cm$^{-1}$, crossing of Re($\sigma_{CC}/\sigma_n$) occurs below the gap as the normal-volume fraction increases. In the intermediate regime where flux flow and flux pinning are difficult to distinguish, e.g., the case $\omega_0 = 30$ cm$^{-1}$, we do not see a clear dip feature in Re($\sigma_{CC}/\sigma_n$) around the gap.
Figure 5-15. Effective optical conductivity calculated from the Coffey-Clem model. The first row shows the real and imaginary parts for three values of depinning frequency $\omega_0$, calculated at the normal-volume fraction $f = 0.4$. The second row shows results for the same quantities at $f = 0.8$.

In conclusion, we measured far-infrared transmission and reflection of NbTiN and NbN thin films in the vortex state when the field was perpendicular to the samples. Significant weakening of superconductivity was observed in both samples. The real and imaginary parts of the optical conductivity have been extracted. The optical conductivity data can be described reasonably well by Maxwell-Garnett theory, showing features
which cannot be accounted for by Bruggeman effective medium approximation and the 
Coffey-Clem model.

When Maxwell-Garnett theory is used to analyze the field-dependent optical 
conductivity, if the superconducting state outside of the vortex cores is assumed to be 
unperturbed by the external field, the fits yield less weakening of superconductivity than 
shown in the data. Inclusion of the pair-breaking effects improves the quality of the fits. 
This leads to the conclusion that the applied magnetic field not only creates normal cores 
in the vortices, but also induces pair-breaking effects on the superconducting fraction 
outside of the vortices.
CHAPTER 6
TIME-RESOLVED MAGNETO-SPECTROSCOPY OF CHARGE DYNAMICS

6.1 Introduction to Non-Equilibrium Superconductivity

When superconductors are subject to external excitations such as photons, phonons, and injected quasiparticle currents, the paired electrons forming the condensate are broken into high-energy quasiparticles. These quasiparticles far above the Fermi level equilibrate among themselves within femtoseconds, and then relax to the superconducting gap edge through electron-electron, electron-phonon scattering within picoseconds. The gap-edge quasiparticles finally recombine to form pairs and emit energy as phonons [138–140]. These recombination-generated phonons were central to the study because they can break additional Cooper pairs before they escape from the superconductor to the surroundings, dominating the effective quasiparticle lifetime [141–144]. Figure 6-1 illustrates the whole process. The relaxation process has been widely studied in BCS superconductors to test non-equilibrium theories of many-body systems [55–57], and in high-temperature superconductors to gain new perspective of their pairing mechanism [58–61].

Experimentally, Testardi showed that strong laser excitations could drive superconducting thin films normal, and that this effect was not due to lattice heating [145]. To explain this phenomenon, Owen and Scalapino [146] proposed an effective chemical potential model to describe the non-equilibrium state. They argued that the energy distribution of the non-equilibrium quasiparticles is characterized by the lattice temperature $T$ and an additional chemical potential $\mu^*$. This model predicts a first-order phase transition to the normal state at a sufficiently large density of excess quasiparticles. Debating that this transition was not observed in experiments, Parker [147] proposed a modified heating theory, in which the non-equilibrium state is characterized by a modified temperature $T^*$ determined by the phonons with energy greater than the optical gap. The two models are indistinguishable in the low perturbation limit.
Figure 6-1. Illustration of the quasiparticle relaxation process.

The recombination process was theoretically studied further by considering the distributions of quasiparticles and phonons. Kaplan et al. [148] calculated the quasiparticle scattering, recombination, and branch-mixing lifetimes and phonon pair-breaking and scattering lifetimes in the near-equilibrium condition, under the assumption that quasiparticles and phonons obey the same distributions as in thermal equilibrium. Beginning with the coupled quasiparticle and phonon kinetic equations and the BCS gap equation, Chang and Scalapino [149] obtained the modified quasiparticle and phonon distributions and the change in the gap parameter. Experimentally the recombination process was investigated through the dependence of the quasiparticle lifetimes on temperature, thin film thickness and excitation strength [150, 151].

6.2 Motivation

An open question is how an external magnetic field could change the recombination process. In Chapter 4 and Chapter 5 we observed the effects of the parallel and perpendicular magnetic fields on the optical properties of thin film superconductors. In this chapter we will investigate how these effects could affect the quasiparticle recombination dynamics in these samples. We report a time-resolved spectroscopic experiment that uses external
magnetic fields to manipulate the quasiparticle recombination. We find that the magnetic field allows us to tune the recombination rate. Such phenomenon is explained through field-induced pair breaking.

6.3 Experimental

The quasiparticle recombination dynamics in the NbTiN and NbN thin-film superconductors is studied by time-resolved pump-probe spectroscopy. Specifics of this technique are discussed in Section 3.2. A pump beam with photon energy greater than the superconducting gap excites the sample and generates quasiparticles; a probe beam measures the sample’s modified optical properties due to the excited quasiparticles at different delay time relative to the arrival of the pump beam. Our experiments were performed using a novel pump-probe set-up illustrated in Figure 3-3. The samples were mounted in a 4He Oxford cryostat equipped with a 10 T superconducting magnet. They are photo-excited by near-infrared laser pulses from a Ti:sapphire laser, and probed by far-infrared radiation produced at Beamline U4IR of the National Synchrotron Light Source, Brookhaven National Laboratory. The frequency range of the probe beam (10–100 cm\(^{-1}\)) is optimal for studying type-II superconductors because of their gap energy scales. Utilizing the pulsed feature of the synchrotron radiation, we generated laser pulses that matches the repetition frequency of the synchrotron pulses to excite the samples, and then measured the laser-induced change in the transmission of the synchrotron probe beam through the samples. To improve sensitivity, we employed a differential technique where the pump pulse was phase-modulated so that its arrival time was sinusoidally dithered a small amplitude \(dt\) with respect to the probe beam. The sample response was then the differential change of the transmission signal \(dS/dt\). This signal was detected using a high sensitivity B-doped Si bolometer operating at 1.6 K by pumping the 4He coolant for detecting the far-infrared radiation. Integrating it over time yields the photo-induced transmission \(S(t)\), which closely relates to the photo-induced
Figure 6-2. Typical differential signal (squares) and integrated signal (circles), measured on NbTiN at 1.9 K, 0 T, at low laser fluence.

quasiparticle density [152]. Typical differential signal and integrated signal are shown in Figure 6-2.

6.4 Temperature Dependence

Before discussing the field-dependent phenomena, it is instructive to look at the temperature dependent recombination process because it is better understood. Figure 6-3 shows the temperature-dependent photo-induced transmission of NbTiN in zero magnetic field at a pump laser fluence of 0.37 nJ/cm$^2$. In this low-fluence regime the sample response can be well described as single exponential,

$$ r(t) = Ae^{-t/\tau} $$

(6–1)

for $t > 0$ and zero otherwise, where $A$ is the amplitude of the exponential decay and $\tau$ is the characteristic lifetime. The detected signal $S(t)$ is the convolution of the exponential decay and the synchrotron probe pulse with a Gaussian profile and a pulse width $\sigma$,

$$ p(t) = \frac{1}{\sqrt{2\pi}\sigma}e^{-t^2/(2\sigma^2)} $$

(6–2)

The detected signal is
Figure 6-3. Temperature dependence of the decay for NbTiN measured at 0 T and low laser fluence. The solid lines are fits using Eq. (6–3).

\[ S(t) = (r \ast p)(t) = \int_{-\infty}^{\infty} r(t')p(t - t')dt' \]
\[ = \int_{0}^{\infty} A e^{-t'/\tau} \frac{1}{\sqrt{2\pi}\sigma} e^{-(t-t')^2/2\sigma^2} dt' \]
\[ = \frac{A}{2} \exp\left(\frac{\sigma^2}{2\tau^2} - \frac{t}{\tau}\right) \operatorname{erfc}\left(\frac{\sigma}{\sqrt{2}\tau} - \frac{t}{\sqrt{2}\sigma}\right), \quad (6–3) \]
in which \( \operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-t^2} dt \) is the complementary error function.

Fits using Eq. (6–3) are shown in Figure 6-3 as solid lines, with \( A, \tau \) and \( \sigma \) as the fitting parameters. Table 6-1 lists the values of these fitting parameters.

From the fitted amplitude \( A \) we can estimate the thermal quasiparticle density via \( N_{th} \propto Q^{-1} - 1 \) where \( Q = A/A_{T \rightarrow 0 \text{ K}} \) [153]. We extrapolate the value of \( A \) to 0 K and use

Table 6-1. Fitting parameters for the temperature-dependent decay data of NbTiN

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( A ) (arb. unit)</th>
<th>( \tau ) (ns)</th>
<th>( \sigma ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>4.13</td>
<td>3.58</td>
<td>0.28</td>
</tr>
<tr>
<td>4.2</td>
<td>3.77</td>
<td>2.75</td>
<td>0.29</td>
</tr>
<tr>
<td>5.6</td>
<td>3.65</td>
<td>1.35</td>
<td>0.29</td>
</tr>
<tr>
<td>7.0</td>
<td>2.60</td>
<td>0.60</td>
<td>0.17</td>
</tr>
<tr>
<td>10.1</td>
<td>1.65</td>
<td>0.55</td>
<td>0.28</td>
</tr>
</tbody>
</table>

121
Figure 6-4. Left: temperature dependence of the exponential decay amplitude $A$; the solid line is a quadratic fit, extrapolating to $T = 0$ K with a value of 4.36. Center: The estimated thermal quasiparticle density $N_{th}$; the solid line is a fit using Eq. (6–4). Right: temperature dependence of the lifetime $\tau$.

that as $A_{T \to 0}$. The estimated $N_{th}$ is fitted to [153]

$$N_{th} = N(0) \sqrt{2\pi k_B T} e^{-\Delta/k_B T},$$ (6–4)

with $N(0)$, the electronic density of states per unit cell at the Fermi level, as the fitting parameter. The result is shown in the center panel of Figure 6-4. We used the BCS temperature dependence for the gap $\Delta$. The agreement of the data and the fit indicates that the sample is in the strong phonon-bottleneck regime. The similar compound NbN is expected to be in the same regime. Fits in Figure 6-3 also yield the FWHM (full width at half maximum) of the synchrotron pulses (approximately 2.35$\sigma$), which determines our best time resolution in the time-resolved experiment to be $\sim$300 ps. The data at 7.0 K was taken with the synchrotron in the 7-bunch compressed mode with a narrower pulse width, while other data were taken in the 7-bunch detuned mode.

6.5 Field Dependence: Field Parallel to Sample Surface

To study the effect of magnetic fields on the recombination dynamics, we measured the field dependent photo-induced transmission for NbTiN and NbN at various laser fluences, with the samples submerged under superfluid $^4$He at $T \leq 2$ K to avoid laser heating. The field was applied parallel to the thin film surfaces to minimize the complexity
of vortex dynamics (discussed in Section 4.3.1). The results are shown in Figures 6-5, 6-6 and 6-7.

6.5.1 Exponential-Decay Fit

The semi-log plots in Figures 6-6 and 6-7 show that at low fluence the decay is simple exponential, similar to that shown in Figure 6-3. At high fluence the decay is initially fast, and then slows down as the excess quasiparticles recombine. In both regimes, the slopes of the semi-log plots suggest that the lifetime increases with increasing field. Early studies of non-equilibrium physics in superconducting Sn thin films in parallel magnetic fields near the transition temperature found shortened quasiparticle lifetime with applied field [154, 155].

We found that for NbTiN, the data cannot be fitted with a single exponential decay. We use the following model with two exponential decays to fit the data,

$$S(t) = \frac{A_1}{2} \exp \left( \frac{\sigma^2}{2\tau_1} - \frac{t}{\tau_1} \right) \text{erfc} \left( \frac{\sigma}{\sqrt{2}\tau_1} - \frac{t}{\sqrt{2}\sigma} \right) + \frac{A_2}{2} \exp \left( \frac{\sigma^2}{2\tau_2} - \frac{t}{\tau_2} \right) \text{erfc} \left( \frac{\sigma}{\sqrt{2}\tau_2} - \frac{t}{\sqrt{2}\sigma} \right),$$

which is a convolution of the probe pulse \(p(t)\) given by Eq. (6–2) and a sample response of the form

$$r(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$$

for \(t > 0\) and zero otherwise, where \(A_1\) and \(A_2\) are amplitudes, and \(\tau_1\) and \(\tau_2\) are characteristic lifetimes. Fit of the field-dependent data for NbTiN using this model are shown as solid lines in Figure 6-5, with fitting parameters listed in Table 6-2.

For NbN, the data can be decently described by the single exponential decay model Eq. (6–3). The fits are shown in Figure 6-7 as solid lines, with fitting parameters listed in Table 6-3. The two-exponential-decay model Eq. (6–5) does not significantly improve the fit.

The analysis of NbTiN and NbN data shows some common features, as shown in Figure 6-8 and Figure 6-9. The effective lifetime increases with increasing field, which is
Figure 6-5. NbTiN decay data in parallel fields at various laser fluences and $T \leq 2$ K. The solid lines are fits using Eq. (6–5).
Figure 6-6. NbTiN decay data in parallel fields at various laser fluences and $T \leq 2$ K on semi-log scale.
Figure 6-7. NbN decay data in parallel fields at various laser fluences and $T \leq 2$ K. The right column are the same data shown in the first column plotted on a semi-log scale. The solid lines are fits using Eq. (6-3).
Figure 6-8. Fitting parameters of NbTiN decay data in parallel fields at various laser fluences. From the first row to the last row, the fluences are: 0.37, 0.80, 1.60, 2.67, 5.35, and 10.70 nJ/cm².
Figure 6-9. Fitting parameters of NbN decay data in parallel fields at various laser fluences. From the first row to the last row, the fluences are: 2.35, 4.56, 9.05, and 18.10 nJ/cm$^2$. 
Table 6-2. Fitting parameters for the NbTiN decay data in parallel fields at various fluences

<table>
<thead>
<tr>
<th>Fluence (nJ/cm²)</th>
<th>Field (T)</th>
<th>$A_1$ (arb. unit)</th>
<th>$\tau_1$ (ns)</th>
<th>$A_2$ (arb. unit)</th>
<th>$\tau_2$ (ns)</th>
<th>$\sigma$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.37</td>
<td>0.0</td>
<td>1.722</td>
<td>1.516</td>
<td>2.627</td>
<td>5.281</td>
<td>0.325</td>
</tr>
<tr>
<td>0.37</td>
<td>2.5</td>
<td>1.315</td>
<td>1.186</td>
<td>3.204</td>
<td>4.637</td>
<td>0.316</td>
</tr>
<tr>
<td>0.37</td>
<td>5.0</td>
<td>1.717</td>
<td>1.261</td>
<td>3.285</td>
<td>5.409</td>
<td>0.365</td>
</tr>
<tr>
<td>0.37</td>
<td>7.5</td>
<td>4.413</td>
<td>5.280</td>
<td>0.143</td>
<td>5.281</td>
<td>0.321</td>
</tr>
<tr>
<td>0.37</td>
<td>10.0</td>
<td>0.000</td>
<td>1.460</td>
<td>5.675</td>
<td>6.714</td>
<td>0.303</td>
</tr>
<tr>
<td>0.80</td>
<td>0.0</td>
<td>3.422</td>
<td>0.762</td>
<td>5.499</td>
<td>3.996</td>
<td>0.337</td>
</tr>
<tr>
<td>0.80</td>
<td>2.5</td>
<td>3.918</td>
<td>0.992</td>
<td>4.888</td>
<td>4.467</td>
<td>0.324</td>
</tr>
<tr>
<td>0.80</td>
<td>5.0</td>
<td>4.162</td>
<td>1.558</td>
<td>4.135</td>
<td>5.427</td>
<td>0.356</td>
</tr>
<tr>
<td>0.80</td>
<td>7.5</td>
<td>5.990</td>
<td>3.150</td>
<td>2.184</td>
<td>10.017</td>
<td>0.316</td>
</tr>
<tr>
<td>0.80</td>
<td>10.0</td>
<td>9.016</td>
<td>4.947</td>
<td>0.897</td>
<td>10.046</td>
<td>0.296</td>
</tr>
<tr>
<td>1.60</td>
<td>0.0</td>
<td>7.625</td>
<td>0.674</td>
<td>8.693</td>
<td>3.385</td>
<td>0.338</td>
</tr>
<tr>
<td>1.60</td>
<td>2.5</td>
<td>7.535</td>
<td>0.834</td>
<td>7.328</td>
<td>4.019</td>
<td>0.318</td>
</tr>
<tr>
<td>1.60</td>
<td>5.0</td>
<td>9.364</td>
<td>1.214</td>
<td>6.325</td>
<td>5.541</td>
<td>0.349</td>
</tr>
<tr>
<td>1.60</td>
<td>7.5</td>
<td>7.004</td>
<td>1.032</td>
<td>10.137</td>
<td>4.923</td>
<td>0.331</td>
</tr>
<tr>
<td>1.60</td>
<td>10.0</td>
<td>12.535</td>
<td>3.372</td>
<td>3.810</td>
<td>10.150</td>
<td>0.293</td>
</tr>
<tr>
<td>2.67</td>
<td>0.0</td>
<td>14.488</td>
<td>0.510</td>
<td>12.660</td>
<td>3.000</td>
<td>0.338</td>
</tr>
<tr>
<td>2.67</td>
<td>2.5</td>
<td>21.461</td>
<td>0.355</td>
<td>11.929</td>
<td>3.083</td>
<td>0.429</td>
</tr>
<tr>
<td>2.67</td>
<td>5.0</td>
<td>14.690</td>
<td>1.024</td>
<td>9.290</td>
<td>4.381</td>
<td>0.346</td>
</tr>
<tr>
<td>2.67</td>
<td>7.5</td>
<td>13.475</td>
<td>0.970</td>
<td>12.772</td>
<td>4.748</td>
<td>0.325</td>
</tr>
<tr>
<td>2.67</td>
<td>10.0</td>
<td>19.987</td>
<td>2.701</td>
<td>5.195</td>
<td>10.018</td>
<td>0.289</td>
</tr>
<tr>
<td>5.35</td>
<td>0.0</td>
<td>31.262</td>
<td>0.467</td>
<td>19.548</td>
<td>2.328</td>
<td>0.333</td>
</tr>
<tr>
<td>5.35</td>
<td>2.5</td>
<td>38.715</td>
<td>0.381</td>
<td>18.490</td>
<td>2.580</td>
<td>0.414</td>
</tr>
<tr>
<td>5.35</td>
<td>5.0</td>
<td>29.605</td>
<td>0.878</td>
<td>13.523</td>
<td>3.752</td>
<td>0.344</td>
</tr>
<tr>
<td>5.35</td>
<td>7.5</td>
<td>23.343</td>
<td>0.857</td>
<td>18.235</td>
<td>3.610</td>
<td>0.321</td>
</tr>
<tr>
<td>5.35</td>
<td>10.0</td>
<td>33.092</td>
<td>2.133</td>
<td>7.169</td>
<td>10.036</td>
<td>0.289</td>
</tr>
<tr>
<td>10.70</td>
<td>0.0</td>
<td>54.718</td>
<td>0.354</td>
<td>36.185</td>
<td>1.439</td>
<td>0.339</td>
</tr>
<tr>
<td>10.70</td>
<td>2.5</td>
<td>69.706</td>
<td>0.384</td>
<td>27.404</td>
<td>2.177</td>
<td>0.402</td>
</tr>
<tr>
<td>10.70</td>
<td>5.0</td>
<td>64.169</td>
<td>0.438</td>
<td>29.746</td>
<td>2.299</td>
<td>0.371</td>
</tr>
<tr>
<td>10.70</td>
<td>7.5</td>
<td>40.623</td>
<td>0.630</td>
<td>29.741</td>
<td>2.574</td>
<td>0.332</td>
</tr>
<tr>
<td>10.70</td>
<td>10.0</td>
<td>41.995</td>
<td>0.861</td>
<td>30.822</td>
<td>3.706</td>
<td>0.312</td>
</tr>
</tbody>
</table>

already evident in the semi-log plot of the raw data. For NbTiN, both the fast and the slow components decay slower when the field is increased. There is no clear trend in the field dependence of the decay amplitudes. It might be decreasing as the field increases, especially for NbN at high fluence.
Table 6-3. Fitting parameters for the NbN decay data in parallel fields at various fluences

<table>
<thead>
<tr>
<th>Fluence (nJ/cm²)</th>
<th>Field (T)</th>
<th>A (arb. unit)</th>
<th>τ (ns)</th>
<th>σ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.35</td>
<td>0.0</td>
<td>6.222</td>
<td>1.989</td>
<td>0.303</td>
</tr>
<tr>
<td>2.35</td>
<td>2.0</td>
<td>5.958</td>
<td>2.113</td>
<td>0.305</td>
</tr>
<tr>
<td>2.35</td>
<td>4.0</td>
<td>6.277</td>
<td>3.036</td>
<td>0.318</td>
</tr>
<tr>
<td>2.35</td>
<td>6.0</td>
<td>5.946</td>
<td>3.120</td>
<td>0.313</td>
</tr>
<tr>
<td>4.56</td>
<td>0.0</td>
<td>11.243</td>
<td>1.640</td>
<td>0.308</td>
</tr>
<tr>
<td>4.56</td>
<td>2.0</td>
<td>10.506</td>
<td>2.264</td>
<td>0.286</td>
</tr>
<tr>
<td>4.56</td>
<td>4.0</td>
<td>10.997</td>
<td>2.482</td>
<td>0.313</td>
</tr>
<tr>
<td>4.56</td>
<td>6.0</td>
<td>11.209</td>
<td>2.458</td>
<td>0.348</td>
</tr>
<tr>
<td>9.05</td>
<td>0.0</td>
<td>21.324</td>
<td>1.398</td>
<td>0.304</td>
</tr>
<tr>
<td>9.05</td>
<td>2.0</td>
<td>20.934</td>
<td>1.473</td>
<td>0.342</td>
</tr>
<tr>
<td>9.05</td>
<td>4.0</td>
<td>19.526</td>
<td>1.988</td>
<td>0.308</td>
</tr>
<tr>
<td>9.05</td>
<td>6.0</td>
<td>19.244</td>
<td>2.016</td>
<td>0.333</td>
</tr>
<tr>
<td>18.10</td>
<td>0.0</td>
<td>35.145</td>
<td>1.265</td>
<td>0.308</td>
</tr>
<tr>
<td>18.10</td>
<td>2.0</td>
<td>36.534</td>
<td>1.288</td>
<td>0.326</td>
</tr>
<tr>
<td>18.10</td>
<td>4.0</td>
<td>32.378</td>
<td>1.734</td>
<td>0.280</td>
</tr>
<tr>
<td>18.10</td>
<td>6.0</td>
<td>31.963</td>
<td>1.764</td>
<td>0.283</td>
</tr>
<tr>
<td>18.10</td>
<td>8.0</td>
<td>30.839</td>
<td>1.923</td>
<td>0.292</td>
</tr>
<tr>
<td>18.10</td>
<td>10.0</td>
<td>29.343</td>
<td>2.187</td>
<td>0.289</td>
</tr>
</tbody>
</table>

6.5.2 Universal Scaling Behavior

The field dependence of the quasiparticle recombination can be demonstrated more clearly by defining an effective instantaneous relaxation rate from the differential signal $dS/dt$ and the integrated signal $S$ at the same delay time $t$,

$$
\tau_{\text{eff}}^{-1} \equiv -\frac{1}{S} \frac{dS}{dt}.
$$

(6–7)

For each set of data at a given condition (same field and same laser fluence), we skip the first few points where the behavior is dominated by the Gaussian probe beam profile; the rest is used to define the effective rate $\tau_{\text{eff}}^{-1}$. We found that at each field $\tau_{\text{eff}}^{-1}$ scales almost linearly with $S$. Moreover, at each field, when plotting $\tau_{\text{eff}}^{-1}$ vs $S$, data at different fluence overlap very well, showing a universal scaling behavior. The results for both samples are shown in Figure 6-10. The $\tau_{\text{eff}}^{-1}$ data are slightly smoothed with the moving average method so that the linear behavior becomes clear. However, curvatures exist in the plots shown in Figure 6-10, especially when $S$ is large, which corresponds to high fluence or the
Figure 6-10. Effective instantaneous relaxation rate for NbTiN and NbN in parallel fields. For NbTiN, data at each field include fluence ranging from 0.37 to 10.70 nJ/cm$^2$. For NbN, data at 8 T and 10 T are only at the fluence of 18.10 nJ/cm$^2$, but range from 2.35 to 18.10 nJ/cm$^2$ at other fields. The straight lines are linear fits to the data.

initial stage of quasiparticle recombination. Note that in Figure 6-10, for a decay trace at a given field and fluence, $\tau_{\text{eff}}^{-1}$ appears at higher $S$ at the initial stage of the recombination. As recombination continues, $S$ decreases, and $\tau_{\text{eff}}^{-1}$ moves towards smaller $S$ on the straight line. For a given field, $\tau_{\text{eff}}^{-1}$ at different laser fluence starts at different level on the straight line. In the following, we will discuss the field dependence shown in Figure 6-10.

6.5.3 Recombination Model

In this section we propose a recombination model to explain the field dependence shown in Figure 6-10.

The quasiparticle recombination in a superconductor including phonon bottleneck effect was first discussed in a phenomenological theory by Rothwarf and Taylor [141] using two coupled rate equations,

$$\frac{dN}{dt} = I_0 - \alpha N^2 + \tau_B^{-1} n,$$  \hspace{1cm} (6-8)

$$\frac{dn}{dt} = J_0 - \frac{1}{2} \tau_B^{-1} n + \frac{1}{2} \alpha N^2 - \tau_{\gamma}^{-1} (n - n_{\text{th}}).$$  \hspace{1cm} (6-9)
Here $N$ and $n$ are the densities of quasiparticles and high-energy phonons, $I_0$ and $J_0$ are the injection rates of quasiparticles and high-energy phonons into the system, $\alpha$ is the intrinsic quasiparticle recombination rate coefficient, and $\tau_B^{-1}$ is the rate of pair breaking by the high-energy phonons. The last term in Eq. (6–9) represents the phonon escaping process, in which $n_{\text{th}}$ is the high-energy phonon density at thermal equilibrium, and $\tau_{\gamma}^{-1}$ is the phonon escaping rate. The quadratic terms in these two equations is based on the fact that two quasiparticles need to be present for a recombination to happen. The coefficients $1/2$ in Eq. (6–9) are included for the reason that when two quasiparticles recombine, only one high-energy phonon is created.

In principle, these two coupled non-linear equations are difficult to solve. However we are more interested in the quasiparticles, because their recombination gives rise to the change of optical properties observed in our experiments. We propose a simpler model that can capture the nature of bimolecular recombination shown by Eq. (6–8), meanwhile taking into account the phonon bottleneck effect. In a superconductor, when quasiparticles recombine, a spin-up quasiparticle and a spin-down quasiparticle need to be available, just like the case of electron-hole recombination in a semiconductor. Motivated by this analogy, we use an equation similar to the band-to-band recombination equation in a semiconductor to describe the quasiparticle recombination,

$$\frac{dN}{dt} = \frac{dN^\uparrow}{dt} + \frac{dN^\downarrow}{dt} = -2R \left( N^\uparrow N^\downarrow - N_{\text{th}}^\uparrow N_{\text{th}}^\downarrow \right). \quad (6–10)$$

Here $N$ is the total quasiparticle number density as in Eqs. (6–8) and (6–9), which consists of spin-up and spin-down populations, $N = N^\uparrow + N^\downarrow$. Similarly $N_{\text{th}} = N_{\text{th}}^\uparrow + N_{\text{th}}^\downarrow$ for the thermal density $N_{\text{th}}$. The phonon bottleneck effect is introduced into the model through the recombination rate coefficient $R$. The above equation is based on the observation that because the recombination requires the presence of two quasiparticles of opposite spin, the recombination rate is expected to be proportional to the product of $N^\uparrow$ and $N^\downarrow$. Noting
that at thermal equilibrium there should be no net change of the quasiparticle density, a thermal term \( N_{\text{th}}^\uparrow N_{\text{th}}^\downarrow \) should be subtracted from \( N^\uparrow N^\downarrow \).

Eq. (6–10) can be rewritten by using the following relations. Firstly, \( N \) consists of the thermal density \( N_{\text{th}} \) and the excess density \( N_{\text{ex}} \), \( N = N_{\text{th}} + N_{\text{ex}} \). Secondly, by defining the spin-up and spin-down quasiparticle fractions \( P^\uparrow \) and \( P^\downarrow \), the corresponding density can be expressed as \( N^\uparrow = P^\uparrow N \) and \( N^\downarrow = P^\downarrow N \). At a constant temperature where the thermal term does not vary with time, Eq. (6–10) can be rewritten as

\[
-\frac{1}{N_{\text{ex}}} \frac{dN_{\text{ex}}}{dt} = 2R(P^\uparrow P^\downarrow)(N_{\text{ex}} + 2N_{\text{th}}).
\]

This ordinary differential equation can be solved exactly, with the following solution,

\[
N_{\text{ex}}(t) = N_{\text{ex},0} \frac{2e^{-t/\tau_1}}{2 + \frac{N_{\text{ex},0}}{N_{\text{th}}} (1 - e^{-t/\tau_1})},
\]

where \( N_{\text{ex},0} = N_{\text{ex}}(t = 0) \), and \( \tau_1 = 1/4RN_{\text{th}}(P^\uparrow P^\downarrow) \). At low fluence, \( N_{\text{ex},0}/N_{\text{th}} \ll 1 \). The solution reduces to a single exponential, with a lifetime given by \( \tau_1 \). At high fluence, Eq. (6–12) predicts a fast decay follow by a slow decay. Numerical results are compared in Figure 6-11. These features are consistent with our data, shown in Figure 6-6 and Figure 6-7. Eq. (6–12) can therefore be used to fit these data using the convolution model. But the fit requires simultaneously adjusting two parameters, the ratio \( N_{\text{ex},0}/N_{\text{th}} \) and the lifetime \( \tau_1 \), which makes it difficult to settle the value for either of them. Instead of performing such a fit, we decided to focus on the scaling behavior shown in Figure 6-10.

To link our measured quantity to the recombination model Eq. (6–11), we assume the photo-induced transmission \( S(t) \) measured at each delay time is proportional to the photo-induced excess quasiparticle density, \( S(t) = CN_{\text{ex}} \), where \( C \) is a constant of proportionality. A more precise definition of \( C \) is \( r(t) = CN_{\text{ex}} \) where \( r(t) \) is the sample response function. However when making Figure 6-10 we have skipped the initial part of the trace characterizing the Gaussian probe beam. \( r(t) \rightarrow S(t) \) in this limit. The
Figure 6-11. Exact solution Eq. (6–12) of the recombination equation at various fluences, plotted on linear scale (left) and semi-log scale (right). At high fluence, this solution predicts a fast decay followed by a slow decay.

The recombination equation can be further written as

\[-\frac{1}{S} \frac{dS}{dt} = 2 \frac{R}{C}(P^\uparrow P^\downarrow)(S + 2S_{th}),\]  

(6–13)

where \(S_{th} = CN_{th}\). The quantity on the left of Eq. (6–13), \(-dS/dt)/S\), is the effective instantaneous relaxation rate \(\tau_{\text{eff}}^{-1}\) we defined in the previous section. Eq. (6–13) is consistent with Figure 6-10, if the field dependence in the figure can be accounted for by the coefficient \(2(R/C)(P^\uparrow P^\downarrow)\).

Note that the data in Figure 6-10 deviate from the straight lines in the high-fluence limit when \(S\) is large, possibly because the high-fluence laser pulses break a significant amount of Cooper pairs, which induces further weakening of the superconductivity [145, 146]. We would like to interpret the field-dependent linear behavior, therefore focus on the low fluence data in the following discussion. In the slope \(2R(P^\uparrow P^\downarrow)/C\) in Eq. (6–13), the constant \(C\) is essentially independent of field. We will discuss the field dependence of \(P^\uparrow P^\downarrow\), \(R\), and \(C\) separately in the following three sections.
6.5.3.1 Recombination rate coefficient

The recombination rate coefficient \( R \) describes the rate of recombination, with the phonon bottleneck effects included. This section discusses its field dependence in the pair-breaking limit.

The quasiparticles, interacting with phonons in the system, fully decay with an effective rate \( \tau^{-1} \). In the low-fluence limit, Gray linearized the Rothwarf-Taylor equations to derive an effective rate [156, 157],

\[
\tau^{-1} = \frac{1}{2} \left( p - \sqrt{p^2 - 8\tau_R^{-1}\tau_\gamma^{-1}} \right),
\]

(6–14)

where \( p = 2\tau_R^{-1} + \tau_B^{-1}/2 + \tau_\gamma^{-1} \). Here \( \tau_R^{-1} \) is the intrinsic recombination rate, \( \tau_B^{-1} \) is the phonon pair-breaking rate, and \( \tau_\gamma^{-1} \) is the phonon escaping rate. The phonon escaping rate is determined by the thin film thickness and the acoustic match between the film and the environment [158], and is therefore field independent. For a film of a few nanometers on a dielectric substrate, it is typically on the order of hundreds of picosecond [159]. We assume for our samples it is about 300 ps. The intrinsic recombination rate \( \tau_R^{-1} \) and phonon pair-breaking rate \( \tau_B^{-1} \) are discussed by Kaplan et al. [148] under near-thermal-equilibrium condition,

\[
\tau_R^{-1}(\Omega) = \frac{\tau_0^{-1}}{(kT_c)^3} \int_{\omega+\Delta}^{\infty} d\Omega \frac{\Omega - \omega}{\sqrt{(\Omega - \omega)^2 - \Delta^2}} \left[ 1 + \frac{\Delta^2}{\Omega - \omega} \right] [n(\Omega) + 1] f(\Omega - \omega),
\]

(6–15)

\[
\tau_B^{-1}(\Omega) = \frac{\tau_{0,ph}}{\pi \Delta_0} \int_{\Delta}^{\Omega - \Delta} d\omega \frac{\omega}{\sqrt{\omega^2 - \Delta^2}} \frac{\Omega - \omega}{\sqrt{(\Omega - \omega)^2 - \Delta^2}} \left[ 1 + \frac{\Delta^2}{\Omega - \omega} \right] [1 - f(\omega) - f(\Omega - \omega)],
\]

(6–16)

where \( f \) and \( n \) are the Fermi-Dirac and Bose-Einstein distribution functions, respectively. \( \tau_0 \) and \( \tau_{0,ph} \) are the characteristic lifetimes of the quasiparticles and phonons,

\[
\tau_0 = \frac{\hbar Z_1(0)}{2\pi b(k_B T_c)^3},
\]

(6–17)

\[
\tau_{0,ph} = \frac{\hbar N}{4\pi^2 N(0) \langle \alpha^2 \rangle_{av} \Delta_0}.
\]

(6–18)
$Z_1(0)$ is the quasiparticle renormalization factor, which is about 2.5. $N$ is the density of ions. Using the mass density of NbN (8.38 g/cm$^3$ from Ref. [160]) and its molecular mass (64.95 from Ref. [161]), we estimate $N \approx 7.78 \times 10^{22}$ cm$^{-3}$. $N(0)$ is the normal-state quasiparticle density of states at the fermi level, which is approximately $2.00 \times 10^{28}$ states/m$^3$·eV for NbN [81]. $b$ and $\langle \alpha^2 \rangle_{av}$ are from the electron-phonon spectral function $\alpha^2(\Omega)F(\Omega)$, where $\alpha^2(\Omega)$ is the square of the matrix element of the electron-phonon interaction, and $F(\Omega)$ is the phonon density of states. $\langle \alpha^2 \rangle_{av}$ is defined by Kaplan et al. as

$$\langle \alpha^2 \rangle_{av} \equiv \frac{1}{3} \int_0^{\infty} \alpha^2(\Omega)F(\Omega)d\Omega. \quad (6-19)$$

Using the tunneling $\alpha^2(\Omega)F(\Omega)$ data for NbN [162], we find $\langle \alpha^2 \rangle_{av} \approx 5.11$ meV. The factor $b$ is introduced by assuming that the electron-phonon spectral function has the form $\alpha^2(\Omega)F(\Omega) = b\Omega^2$. According to Eq. (6–19),

$$\langle \alpha^2 \rangle_{av} = \frac{1}{3} \int_0^{\infty} \alpha^2(\Omega)F(\Omega)d\Omega \approx \frac{1}{3} \int_0^{k_B\Theta_D} b\Omega^2d\Omega = \frac{1}{9} b(k_B\Theta_D)^3, \quad (6-20)$$

where $\Theta_D$ is the Debye temperature, which is approximately 331 K for NbN [163]. From the above equation, we estimate $b \approx 1.98 \times 10^{-3}$ meV$^{-2}$. From Table 3-1 we have $T_c = 12.8$ K and $\Delta_0 = 17.9$ cm$^{-1}$ for NbN. With these parameters, we estimate from Eqs. (6–17) and (6–18) that $\tau_0 \approx 9.84 \times 10^{-11}$ s and $\tau_{0,ph} \approx 7.99 \times 10^{-12}$ s. NbTiN should have similar material parameters. Using all the same parameters except for $T_c$ and $\Delta_0$, which we take from Table 3-1, we estimate for NbTiN $\tau_0 \approx 1.94 \times 10^{-10}$ s and $\tau_{0,ph} \approx 1.12 \times 10^{-11}$ s.

Note that Eqs. (6–15) and (6–16) involve the gap $\Delta$, the quasiparticle density of states, and the coherence factor. When a magnetic field is applied parallel to the thin films, the pair-breaking effects could affect all of them. We replace the $\Delta$ in the integration limits by the half effective spectroscopic gap $\Omega_G$. The modified quasiparticle density of states is given by Eq. (4–32) as a function of the pair-breaking parameter. We did not find explicit discussions of the coherence factor in the pair-breaking limit. As a
first order approximation, we assume this factor still takes the same form, but with $\Delta$ replaced by $\Omega_G$. We consider the quasiparticles at the gap edge with energy $\omega = \Omega_G$, and the phonons just energetic enough to break more pairs (take $\Omega = 2.001\Omega_G$ for the convenience of calculation). The calculated lifetimes are compared in Figure 6-12. At zero field, $\tau_B$ is comparable to $\tau_\gamma$, both being smaller than $\tau_R$. As the field increases, the induced pair-breaking effects drastically increase $\tau_B$, making it much greater than $\tau_R$ and $\tau_\gamma$. The phonon escaping rate is much faster than the phonon pair-breaking rate, so that the phonon bottleneck becomes unimportant. The effective lifetime is dominated by the intrinsic recombination time $\tau_R$.

In the low fluence limit, assuming no spin polarization, we have from Eq. (6–11) that

$$\tau_{\text{eff}}^{-1} \approx RN_{\text{th}}. \quad (6–21)$$

This equation together with Eq. (6–14) yields

$$R = \frac{\tau^{-1}}{N_{\text{th}}}, \quad (6–22)$$

where

$$N_{\text{th}} = 2 \int_0^{\infty} N(E)f(E), \quad (6–23)$$

with the single-spin quasiparticle density of states $N(E)$ given by Eq. (4–32). The $\Omega_G$ dependence of $N_{\text{th}}$ as well as $R$ are plotted in Figure 6-12 in the second column, with the latter showing an almost quadratic relation.

### 6.5.3.2 Spin-polarization factor

The spin-polarization factor $P^\uparrow P^\downarrow$ will strongly depend on the magnetic field if the field mainly acts on the electron spin, requiring the spin-orbit scattering to be negligible. This corresponds to the Pauli paramagnetic limit. According to the BCS theory, electrons form spin-singlet pairs condensed in the ground state; the spin susceptibility vanishes as the temperature approaches 0. A great amount of work on superconductor spin susceptibility was done on thin films samples with thickness so small that the effect
Figure 6-12. First column: the calculated intrinsic recombination time $\tau_R$, phonon pair-breaking time $\tau_B$, and the effective lifetime $\tau$ as a function of $\Omega_G$. The phonon escaping time $\tau_\gamma$ is taken to be 0.3 ns. Second column: thermal quasiparticle density $N_{th}$ and the recombination rate coefficient $R$ as a function of $\Omega_G$.

of a magnetic field on the electron orbits can be neglected. Paramagnetic splitting of the quasiparticle density of states was observed in 5 nm aluminum films in a parallel magnetic field [14]. van Bentum and Wyder [93] studied far-infrared absorption of thin superconducting aluminum films with different thicknesses in parallel magnetic field. They found that 10 nm thin films are in the pair-breaking limit, while ultrathin films less than 5 nm are in the paramagnetic limit.
Figure 6-13. Majority spin fraction of NbTiN and NbN in the paramagnetic limit. The circles and squares are extracted from the slopes in Figure 6-10, all scaled so that the majority spin fraction is 1/2 at 0 T. The solid and dashed lines are theoretical calculations using Eqs. (6–24), (6–25), and (6–26).

In the low-fluence limit, the excess quasiparticle density is small compared to the thermal population. The majority spin fraction $P^\downarrow$ can be calculated from the paramagnetic model, using Fermi-Dirac distribution of quasiparticles $f(E)$ and the quasiparticle density of states $\text{DOS}(E)$ from the BCS theory,

$$N^\downarrow = 2 \int_0^\infty f(E)\text{DOS}(E + \mu_B H) dE,$$
$$N^\uparrow = 2 \int_0^\infty f(E)\text{DOS}(E - \mu_B H) dE.$$  \hspace{1cm} (6–24)  \hspace{1cm} (6–25)

From these, $P^\downarrow$ can be calculated as

$$P^\downarrow = \frac{N^\downarrow}{N^\uparrow + N^\downarrow}.$$  \hspace{1cm} (6–26)

On the other hand, if we assume that the field dependence we see in Figure 6-10 is only through the product $P^\uparrow P^\downarrow$, we can extract the majority spin fraction at different fields. The results are compared with the calculation using Eq. (6–26) in Figure 6-13.
Apparently, Pauli paramagnetism gives more polarization than what the data show. This could be due to the strong spin-orbit scattering in NbTiN and NbN. Tedrow and Meservey observed the spin-state mixing in thin aluminum films due to spin-orbit scattering [164]. They defined a spin-orbit scattering parameter $b \equiv \frac{\hbar}{3\tau_{so}}\Delta$ to describe the strength of spin-orbit scattering. They calculated that as $b$ is increased to 0.5, the spin-up and spin-down quasiparticle density of states mix up completely, leaving no clear signature of the two-peak feature in the density of states due to Zeeman splitting. We found for a similar compound NbTi, $\tau_{so} = 3.0 \times 10^{-14}$ s [66]. Using the $\Delta_0$ of NbTiN and NbN, we estimated that $b = 4.2$ and 3.3 for NbTiN and NbN, respectively. This indicates strong spin-state mixing in the NbTiN and NbN samples, if their spin-orbit scattering time $\tau_{so}$ is close to that of NbTi. Based on these arguments, we expect that the spin polarization factor $P^\uparrow P^\downarrow$ is weakly dependent on the field.

### 6.5.3.3 Constant of proportionality

The “constant” of proportionality $C$ introduced through $S = CN_{ex}$ cannot be perfectly field independent under all conditions. The photo-induced transmission $S(t)$ measured at different fields are related to the field-dependent transmission shown in Figure 4-2. The excess quasiparticle density $N_{ex}$ depends on the field-dependent energy gap $\Omega_G$. The “constant” $C$, defined as the ratio $S/N_{ex}$, is possibly also field dependent. In this section we will show that $C$ is almost field-independent in the low fluence regime.

Assume that all the laser energy is eventually distributed to the gap-edge quasiparticles after relaxation. For a laser pulse with fluence $F$ illuminated on a thin film sample area $a$ with film thickness $d$, the maximum excess quasiparticle density is

$$N_{ex,max} = \frac{F \cdot a \cdot \eta/\Omega_G}{a \cdot d} = \frac{F\eta}{\Omega_Gd}.$$  \hspace{1cm} (6–27)

Here $\eta$ is the percentage of laser power that eventually goes into the photo-excitation process. It consists of three factors, all evaluated at the laser frequency (near-infrared). The first factor is the transmittance of quartz window on the magnet, which is about
90% [165]. The second factor is the reflectance of the aluminum mirror that directs laser beam onto the sample (left panel of Figure 4-1), which is about 88% [166]. The third factor is the absorption of the thin film superconductor, which is about 30%, calculated as $1 - T_s - R_s$. Therefore $\eta = 24\%$. As an estimate, at 10.7 nJ/cm$^2$, for NbTiN at 2 K and 0 T, $\Omega_G = 14.3$ cm$^{-1}$ and $d = 10$ nm, we calculated $N_{ex,max} = 9.03 \times 10^{18}$ cm$^{-3}$. Comparing to the superfluid density we estimated earlier in Section 4.4.6, $n_s = 6.06 \times 10^{19}$ cm$^{-3}$, this is about 14.9% of the total superfluid density $n_s$. At the lowest fluence of 0.37 nJ/cm$^2$, the corresponding percentage is about 0.5%.

We introduced a constant of proportionality $C$ to link the measured photo-induced transmission signal to the excess quasiparticle density, $S = CN_{ex}$. Therefore we have $S_{max} = CN_{ex,max}$. Using Eq. (6–27), this becomes

$$S_{max} = C \cdot \frac{F \eta}{\Omega_G d}$$  \hspace{1cm} (6–28)

Therefore a plot of $S_{max}$ vs $F \eta/\Omega_G d$ (or equivalently $S_{max}$ vs $N_{ex,max}$) at different fields should demonstrate the field dependence of $C$. Such a plot for NbTiN is shown in Figure 6-14. In the calculation, the values of $S_{max}$ are read directly from data, and the values of field dependent $\Omega_G$ are from Table 4-1. The left panel of Figure 6-14 shows a trend of saturation at high fluence. Overall, there is an almost square root relation between $S_{max}$ and $N_{ex,max}$. The traces at various fields differ significantly as $S_{max}$ increases. The low fluence part of the left panel is shown in the right panel. The almost linear relation indicates that $C$ is approximately constant. Traces at different fields overlap reasonably well, suggesting that $C$ is weakly field dependent. This justifies our approximation that in the low fluence regime, where the excess quasiparticle density is much less than the total superfluid density, $S = CN_{ex}$ and $C$ is a constant.

6.5.3.4 Total effect of magnetic fields

Now we have determined that $C$ and $P^\uparrow P^\downarrow$ are almost independent of field. The field dependence of the slope $2(R/C)(P^\uparrow P^\downarrow)$ is dominated by the effective rate $R$. This predicts
Figure 6-14. $S_{\text{max}}$ vs $N_{\text{ex, max}}$ for NbTiN in parallel fields. The ratio between the two is proportional to $C$. The right panel shows the low fluence part of the left panel. The upper scale of the x-axis shows the ratio of $N_{\text{ex, max}}$ and the superfluid density at 0 T, 2 K.

an almost quadratic relation between the slope and the gap. The calculated $R$ vs $\Omega_G$ for both NbTiN and NbN are compared to the slope vs gap data in Figure 6-15, suggesting qualitative agreement. In the left panel of Figure 6-10 only the data with $S$ smaller the magnitude of 20 (i.e., in the low-fluence limit) are used for the extraction of the slope. $\Omega_G$ is the calculated value taken from the solid line in the left panel of Figure 4-9, ignoring the difference between 2 K and 3 K because the gap is fully developed. In the right panel of Figure 6-10 only the data with $S$ smaller the magnitude of 10 are used for the extraction of the slope. The error bars in both plots are the standard deviations of the slope as the fitting parameter of the linear fit in Figure 6-10.

Some issues remain in our interpretations of the field dependence. Although the predicted $R$ vs $\Omega_G$ is consistent with the slope vs $\Omega_G$ data, the predicted effective lifetime vs $\Omega_G$ from the Kaplan-type calculation predicts a different trend from that shown by the decay data. This inconsistency needs to be addressed. The coherence factor in a magnetic field is expected to be modified from the BCS form. Therefore it should be derived in the pair-breaking regime. It would also be useful if higher magnetic fields can be used to suppress the gap even further, so that one can verify what really happens when $\Omega_G$...
Figure 6-15. Circles: slope vs $\Omega_G$ for NbTiN and NbN in parallel fields. The error bars are calculated deviations of the slope from the linear fits in Figure 6-10. Dashed lines: the calculated relation between $R$ and $\Omega_G$, taken from Figure 6-12.

6.6 Field Dependence: Field Perpendicular to Sample Surface

In the previous section, we have seen that the main effect of a parallel magnetic field is to suppress the spectroscopic gap, which results in the slowing of the quasiparticle recombination. What happens if the external magnetic field is applied perpendicular to the sample surface so that vortices are created? Such experiments were performed on the NbTiN and NbN samples using the same pump-probe technique. The photo-induced transmission signal at various magnetic fields and laser fluences are plotted in Figure 6-16 for NbTiN and in Figure 6-17 for NbN. The samples were submerged under superfluid helium ($T \leq 2$ K) to reduce laser heating.
Figure 6-16. NbTiN decay data in perpendicular fields at low and high laser fluences and $T \leq 2$ K. The second row shows the same data in the first row plotted on a semi-log scale.
Figure 6-17. NbN decay data in perpendicular fields at various laser fluences and $T \leq 2$ K. The second column shows the same data in the first column plotted on a semi-log scale.
For NbTiN, the data at low and high fluence show similar features. In Figure 6-16, at low fields, the decay is more or less single exponential. As the field is increased above 8 T, the decay curve clearly changes its shape, indicating that the recombination speeds up as quasiparticles recombine, which is not observed in the parallel field configuration. In both the low and high fluence regimes, the decay seems to slow down as the field increases, which agrees qualitatively with the parallel field configuration.

For NbN, the field dependence at low and high fluence are completely different. The low fluence data (in the first and second row of Figure 6-17) are very similar to those of NbN in the parallel field configuration. The decays are single-exponential like. The recombination is slowed as the field is increased. At high fluence (the third row in Figure 6-17), the decay speeds up as the field increase. This is clearly different from the parallel field configuration, and different from the NbTiN data at high fluence shown in Figure 6-16.

From the measured photo-induced transmission \(S(t)\) and the differential signal \(dS/dt\), we calculated the effective instantaneous recombination rate \(\tau_{\text{eff}}^{-1}\), defined by Eq. (6-7). Plotting it vs the photo-induced transmission at various fluences and fields, we obtained Figure 6-18 for NbTiN and Figure 6-19 for NbN.

For the NbTiN data shown in Figure 6-18, we do not observe the clear linear relation between \(\tau_{\text{eff}}^{-1}\) and \(S\) as in the parallel field configuration, especially at low fluence and low fields. Note that there is a curvature in the data at 1.34 nJ/cm\(^2\) and 0 T. In the parallel field configuration, however, we did not see this feature at 0 T and various fluences. The curvature might be due to the inaccuracy of the data at low values of \(S\). Figure 6-18 is different from the parallel case show in the left panel of Figure 6-10 in two aspects. Firstly, the data at low and high fluences in the two panels of Figure 6-18 do not overlap. Secondly, at high fields (9 T and 10 T), it is clear that the recombination becomes faster as the process continues (note that as the quasiparticles recombine, the photo-induced signal \(S\) decreases). However there is one similarity in the \(\tau_{\text{eff}}^{-1}\) and \(S\) plot between the
parallel and perpendicular field configurations: at a given level of $S$, as the field increase, the effective rate decreases, i.e., the recombination slows down at higher fields.

For the NbN data shown in Figure 6-19, the relation between $\tau_{\text{eff}}^{-1}$ and $S$ is almost linear, similar to the NbN data in the parallel field configuration shown in the right panel of Figure 6-10. At low fluence (0.40 nJ/cm$^2$ and 1.34 nJ/cm$^2$), the field dependence is qualitatively the same as in the parallel field configuration: at a given level of $S$, the effective recombination rate is smaller at higher fields. At high fluence (10.70 nJ/cm$^2$), at the same $S$, the effective recombination rate is higher at higher fields. This is completely different from the cases shown in Figure 6-10 and Figure 6-18. The data at different fluences and the same field in the three panels of Figure 6-19 do not overlap.

These new features in the field dependence suggest different physics involved in the recombination process when vortices are present. They cannot be explained by the recombination model described in Section 6.5.3, therefore require new types of analysis. The faster recombination at higher fields in NbN in the high fluence regime suggests vortices might provide extra channels for the excess phonons to relax.
6.7 Summary

In conclusion we used time-resolved laser-pump synchrotron-probe spectroscopy to study the quasiparticle recombination dynamics in NbTiN and NbN thin films. Parallel and perpendicular magnetic fields were observed to change the recombination process differently.

When a parallel magnetic field was applied, significant slowing of the recombination was observed in both samples. This can be directly seen from the decay traces, or can be explicitly shown by fitting the data with a single-exponential or two-exponential decay model. We interpreted the decay data by defining an effective recombination rate, and found a linear relation between this rate and the photo-induced transmission signal. The slope of the straight lines shows dramatic field dependence. We proposed a recombination model to explain the field dependence. The analysis suggests that the magnetic-field-induced pair-breaking effects modify the quasiparticle density of states and suppress the energy gap. The consequence is a dramatic slowing of the quasiparticle recombination. We did not need to include the effect of the spin-polarization factor on the recombination, probably due to the strong spin-orbit scattering in these materials.

When a perpendicular magnetic field was applied, the two samples show different behaviors. For NbTiN, when the magnetic field is increased above 8 T, in both the low and high fluence regimes the quasiparticle recombination rate increases as the recombination process continues. For NbN, at high fluence, the recombination is faster at high fields. These features are not explained by the recombination model we proposed.
Figure 6-19. Effective instantaneous relaxation rate for NbN in perpendicular fields at low fluence (first and second row) and high fluence (last row).
CHAPTER 7
CONCLUSIONS

In this dissertation, conventional and time-resolved infrared spectroscopy were employed to study the magnetic properties of type-II superconducting thin films of NbTiN and NbN.

The first part (Chapter 4 and Chapter 5) dealt with equilibrium-state properties in magnetic fields. Transmission and reflection measurements were taken at low reduced temperature in both parallel and perpendicular magnetic fields, using high-brightness synchrotron radiation as the source. Optical conductivities were extracted directly from these data.

When the field was applied parallel to the sample surface, we found the optical conductivity significantly modified. The energy gap, shown as the absorption edge in the real part of the optical conductivity, is clearly suppressed due to the magnetic field. Both the optical conductivity and the degree of gap suppression are in good agreement with Abrikosov and Gor’kov’s pair-breaking theory. The data, when compared to the theory, suggest two distinct mechanisms of pair breaking in the two samples. For the 10 nm NbTiN thin film, the order parameter is almost constant throughout the sample. The field, when acting on the electron orbital motion, mainly breaks the time-reversal symmetry of the pairing. We observed that the strength of pair breaking is almost quadratic in field. For the 70 nm NbN film, a parallel magnetic field inevitably creates vortices in the sample, causing spatial variation of the order parameter. Such an effect induces pair breaking with its strength almost linear in field, as confirmed by our analysis. This is the first time that optical absorption has been employed to test quantitatively the theory of pair breaking by an external magnetic field.

When the field was applied perpendicular to the sample surface, we observed more dramatic weakening of superconductivity compared to the parallel-field case. Three models, the Maxwell-Garnett theory, the Bruggeman effective medium approximation,
and the Coffey-Clem model, were used to calculate the effective optical conductivity of a type-II superconductor in the mixed state. Our optical conductivity data clearly rule out the latter two and support the Maxwell-Garnett theory as a decent description of the mixed state. Furthermore, the data of NbN suggest additional weakening of superconductivity other than that caused by vortices. Inclusion of the pair-breaking effects found in Chapter 4 into the Maxwell-Garnett theory makes the model more consistent with the data. These findings lead us to the conclusion that the mixed-state electrodynamic response can be well described by the Maxwell-Garnett theory. Contrary to the general assumption that the superconducting fraction in the vortex state is unperturbed by the external magnetic field, our data show evidence of pair breaking on these superconducting electrons.

The second part (Chapter 6) discussed the non-equilibrium quasiparticle recombination dynamics after photo-excitation, under the influence of magnetic fields. The two samples studied in Chapter 4 and Chapter 5 were excited by infrared laser pulses, and probed with synchronized synchrotron radiation. The photo-excitation-induced transmission change reveals the quasiparticle recombination dynamics in these samples. By applying a parallel magnetic field, we found that the recombination process is significantly slowed. There is a linear relation between the effective recombination rate and the photo-induced transmission signal, with the slope showing strong field dependence. Our recombination model is consistent with the interpretation that the slowing is due to the field-induced pair-breaking effects, which we have established in Chapter 4. The model also suggests another regime where the field dependence is dominated by Pauli spin paramagnetism. We did not need to include such effects to explain our data, probably because of the strong spin-orbit scattering in our samples.

The studies in Chapter 4 on the pair-breaking effects may be further extended. Our study focused on two different types of materials. Clearly, the film thickness is an important parameter that distinguishes different regimes of pair breaking. It would be
interesting to systematically identify different regimes using the same magneto-optical technique present in Chapter 4, by varying the thickness of the same type of material. In general, the same experimental technique and data analysis procedures can be applied to study any kind of superconductor in the form of a thin film on a substrate.

The studies in Chapter 6 can also be refined and extended. In the parallel field configuration, the correct form of the coherence factor in the pair-breaking limit will be useful. It would also be interesting to suppress the gap further, even into the gapless regime. The corresponding effective recombination rate can be useful to verify the validity of our recombination model. The different features observed in the perpendicular field configuration requires new models to understand quasiparticle recombination in the presence of vortices.
APPENDIX A
USEFUL PHYSICAL CONSTANTS AND UNIT CONVERSIONS

Wavenumber $\nu = 1/\lambda$ is predominantly used to denote frequency throughout this dissertation. It is therefore helpful to know the commonly-used units and physical constants expressed in term of wavenumbers.

$$1 \text{ cm}^{-1} = 3 \times 10^{10} \text{ Hz} = 1.9878 \times 10^{-23} \text{ J} = 1.2424 \times 10^{-4} \text{ eV}. \quad (A-1)$$

From this, the Boltzmann constant $k_B = 8.6173 \times 10^{-5} \text{ eV/K} = 0.6936 \text{ cm}^{-1}/\text{K}$, and the Bohr magneton $\mu_B = 5.7884 \times 10^{-5} \text{ ev/T} = 0.4659 \text{ cm}^{-1}/\text{T}$.

Equations throughout this dissertation use Gaussian CGS units. In many occasions, quantities are reported in practical units. A conversion table taken from Ref. [3] is included here for convenience. A particularly useful conversion used in this dissertation is for the optical conductivity. Numerically, $\sigma_{\text{CGS}} = 9 \times 10^{11} \times \sigma_{\text{prac}}$, where $\sigma_{\text{CGS}}$ is in $\text{s}^{-1}$ and $\sigma_{\text{prac}}$ is in practical units $\Omega^{-1}\cdot\text{cm}^{-1}$.

Table A-1. Conversion table for electromagnetic quantities between CGS and SI units.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>CGS</th>
<th>SI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Velocity of light</td>
<td>$c$</td>
<td>$1/\sqrt{\mu_0\varepsilon_0}$</td>
</tr>
<tr>
<td>Magnetic induction</td>
<td>$B$</td>
<td>$\sqrt{4\pi/\mu_0}B$</td>
</tr>
<tr>
<td>Magnetic field</td>
<td>$H$</td>
<td>$\sqrt{4\pi\mu_0}H$</td>
</tr>
<tr>
<td>Magnetization</td>
<td>$M$</td>
<td>$\sqrt{\mu_0/4\pi}M$</td>
</tr>
<tr>
<td>Charge density (or charge, current,</td>
<td>$\rho$</td>
<td>$\rho/\sqrt{4\pi\varepsilon_0}$ (or $Q, I, J, P$)</td>
</tr>
<tr>
<td>current density, polarization)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electric field (or potential, voltage)</td>
<td>$E$ (or $\phi, V$)</td>
<td>$\sqrt{4\pi\varepsilon_0}E$ (or $\phi, V$)</td>
</tr>
<tr>
<td>Displacement</td>
<td>$D$</td>
<td>$\sqrt{4\pi/\varepsilon_0}D$</td>
</tr>
<tr>
<td>Conductivity</td>
<td>$\sigma$</td>
<td>$\sigma/4\pi\varepsilon_0$</td>
</tr>
<tr>
<td>Resistance (or impedance, inductance)</td>
<td>$R$ (or $Z$)</td>
<td>$4\pi\varepsilon_0R$ (or $Z$)</td>
</tr>
<tr>
<td>Inductance</td>
<td>$L$</td>
<td>$4\pi\varepsilon_0L$</td>
</tr>
<tr>
<td>Capacitance</td>
<td>$C$</td>
<td>$C/4\pi\varepsilon_0$</td>
</tr>
<tr>
<td>Permeability</td>
<td>$\mu$</td>
<td>$\mu/\mu_0$</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>$\varepsilon$</td>
<td>$\varepsilon/\varepsilon_0$</td>
</tr>
</tbody>
</table>
APPENDIX B
INTERACTION OF LIGHT WITH MATTER

Discussions of interaction between electromagnetic waves and matter can be found in various textbooks, e.g. [167, 168]. Here a short summary is included for quick reference.

Consider a homogeneous isotropic medium of dielectric constant $\epsilon_1$, permeability $\mu$, and conductivity $\sigma_1$. The subscript “1” is to denote the real part of the quantity; subscript “2” denotes the imaginary part. The material equations relate the electric current density $\mathbf{J}$ to the electric field $\mathbf{E}$, the electric displacement $\mathbf{D}$ to $\mathbf{E}$, and the magnetic induction $\mathbf{B}$ to the magnetic vector $\mathbf{H}$,

\begin{align}
\mathbf{J} &= \sigma_1 \mathbf{E}, \\
\mathbf{D} &= \epsilon_1 \mathbf{E}, \\
\mathbf{B} &= \mu \mathbf{H}.
\end{align}

In the absence of external free charges, the Maxwell’s equations read

\begin{align}
\nabla \cdot \mathbf{D} &= 0, \\
\nabla \cdot \mathbf{B} &= 0, \\
\nabla \times \mathbf{E} &= -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \\
\nabla \times \mathbf{H} &= \frac{4\pi}{c} \mathbf{J} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t}.
\end{align}

Noting the relations Eqs. (B–1)–(B–3) and eliminating $\mathbf{H}$ from Eq. (B–6) using Eq. (B–7) yields the wave equation

\begin{equation}
\nabla^2 \mathbf{E} = \frac{\mu \epsilon_1}{c^2} \ddot{\mathbf{E}} + \frac{4\pi \mu \sigma_1}{c^2} \dot{\mathbf{E}}.
\end{equation}

If we now specialize to the case of monochromatic plane waves of the form $\mathbf{E} = \mathbf{E}_0 e^{i(k\cdot r - \omega t)}$, Eq. (B–8) becomes

\begin{equation}
\nabla^2 \mathbf{E} + \frac{\omega^2 \mu}{c^2} \left( \epsilon_1 + \frac{4\pi i \sigma_1}{\omega} \right) \mathbf{E} = 0.
\end{equation}

154
Define the quantity in the parenthesis of Eq. (B–9) as the complex dielectric constant $\epsilon$,

$$\epsilon = \epsilon_1 + \frac{4\pi i}{\omega} \sigma_1. \tag{B–10}$$

From the wave equation Eq. (B–9) the complex wave vector has its magnitude defined by

$$k^2 = \frac{\omega^2 \mu}{c^2} \epsilon. \tag{B–11}$$

The corresponding complex refractive index is defined as

$$N = n + i\kappa, \tag{B–12}$$

where $n$ is the refractive index and $\kappa$ is the extinction coefficient. Since $N = ck/\omega$,

$$N^2 = \left(\frac{\omega}{c}\right)^2 k^2 = \mu \epsilon = \mu \left(\epsilon_1 + \frac{4\pi i}{\omega} \sigma_1\right). \tag{B–13}$$

Comparing with $N^2 = (n + i\kappa)^2$ we have

$$n^2 - \kappa^2 = \mu \epsilon_1, \tag{B–14}$$

$$2n\kappa = \mu \frac{4\pi \sigma_1}{\omega} \equiv \mu \epsilon_2. \tag{B–15}$$

Therefore

$$\epsilon_1 = \frac{(n^2 - \kappa^2)}{\mu}, \tag{B–16}$$

$$\epsilon_2 = 2n\kappa/\mu = 4\pi \sigma_1/\omega, \tag{B–17}$$

and

$$n = \left[\frac{1}{2} \left(\sqrt{\epsilon_1^2 + \epsilon_2^2 + \epsilon_1}\right)\right]^{1/2}, \tag{B–18}$$

$$\kappa = \left[\frac{1}{2} \left(\sqrt{\epsilon_1^2 + \epsilon_2^2 - \epsilon_1}\right)\right]^{1/2}. \tag{B–19}$$

The imaginary part of the conductivity is defined through the relation

$$\epsilon = 1 + \frac{4\pi i}{\omega} \sigma \tag{B–20}$$
so that

\[ \epsilon_1 = 1 - \frac{4\pi}{\omega} \sigma_2. \] (B–21)

Now consider the propagation of the wave,

\[ E = E_0 e^{i(k \cdot r - \omega t)} = E_0 e^{- \frac{\omega}{c} \hat{k} \cdot r} e^{i\frac{\omega}{c} \hat{k} \cdot r - \omega t}, \] (B–22)

where \( \hat{k} \) is the unit vector along the wave propagation direction. The first exponential term in the above equation describes the attenuation of the electromagnetic waves inside the medium. The absorption coefficient \( \alpha \) is defined as

\[ \alpha = \frac{2\omega}{c} \kappa \] (B–23)

so that the energy of the wave falls to \( 1/e \) after it travels a distance \( 1/\alpha \).

The following table summarizes the relations between these optical constants.

<table>
<thead>
<tr>
<th>( \epsilon = \epsilon_1 + i\epsilon_2 )</th>
<th>( \sigma = \sigma_1 + i\sigma_2 )</th>
<th>( N = n + i\kappa )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon = \epsilon_1 + i\epsilon_2 )</td>
<td>( \sigma_1 = \frac{\omega}{4\pi} \epsilon_2 )</td>
<td>( \epsilon_1 = 1 - \frac{4\pi}{\omega} \sigma_2 )</td>
</tr>
<tr>
<td>( \sigma = \sigma_1 + i\sigma_2 )</td>
<td>( \sigma_2 = \frac{\omega}{4\pi} (1 - \epsilon_1) )</td>
<td>( \epsilon_2 = \frac{4\pi}{\omega} \sigma_1 )</td>
</tr>
<tr>
<td>( N = n + i\kappa )</td>
<td>( n = \left[ \frac{1}{2} \left( \sqrt{\epsilon_1^2 + \epsilon_2^2 + \epsilon_1} \right) \right]^{1/2} )</td>
<td>( n = n(\epsilon_1, \epsilon_2) )</td>
</tr>
<tr>
<td>( \kappa = \left[ \frac{1}{2} \left( \sqrt{\epsilon_1^2 + \epsilon_2^2 - \epsilon_1} \right) \right]^{1/2} )</td>
<td>( n = n(\epsilon_1, \epsilon_2) )</td>
<td>( n = n(\epsilon_1, \epsilon_2) )</td>
</tr>
<tr>
<td>( \kappa = \frac{\omega}{4\pi} \epsilon_2 (n, \kappa) )</td>
<td>( \kappa = \kappa(\epsilon_1, \epsilon_2) )</td>
<td>( \kappa = \kappa(\epsilon_1, \epsilon_2) )</td>
</tr>
<tr>
<td>( \sigma_1 = \frac{\omega}{4\pi} \epsilon_2 (n, \kappa) )</td>
<td>( \sigma_2 = \frac{\omega}{4\pi} \epsilon_2 (n, \kappa) )</td>
<td>( \sigma_2 = \frac{\omega}{4\pi} \epsilon_2 (n, \kappa) )</td>
</tr>
</tbody>
</table>

156
APPENDIX C
THIN FILM OPTICS

Thin film optics is essential in the analysis performed in Chapter 4 and Chapter 5. Detailed derivations of the main equations used in those two chapters will be presented in this appendix.

C.1 Fresnel Equations

Before discussing thin film optics, we will review the classical problem of finding the transmission and reflection coefficients at the boundary of two media. These are solved from the Fresnel equations. The same method will then be used for our problem of thin film on a thick substrate.

The Fresnel equations describe how light transmits and reflects at the interface of two linear, isotropic, and homogeneous media of refractive indices $n_i$ and $n_t$, where the subscripts $i$ and $t$ denote incidence and transmission, respectively. The equations can be found in most standard textbooks on optics, e.g., [169], for s-polarized and p-polarized light (s-polarized refers to polarization perpendicular to the plane of incidence; p-polarized refers to polarization parallel to the plane of incidence). The combination of these two explains any other cases of polarization. The two boundary conditions used in the derivation of the Fresnel equations, i.e., the tangent components of the electric field $\mathbf{E}$ and magnetic field $\mathbf{H}$ with respect to the interface are continuous, are from two of the Maxwell’s equations Eqs. (B–6) and (B–7),

$$\nabla \times \mathbf{E} = -\frac{1}{c} \dot{\mathbf{B}},$$

$$\nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{J}_f + \frac{1}{c} \dot{\mathbf{D}},$$

by integrating them along an infinitesimal Stokesian loop across the interface [170]. Here $\mathbf{J}_f$ is the free charge current density.

Assume the incident, reflected and transmitted waves are all plane waves, $\mathbf{E}_i = \mathbf{E}_{0i} e^{i(k_i \cdot r - \omega_i t)}$, $\mathbf{E}_r = \mathbf{E}_{0r} e^{i(k_r \cdot r - \omega_r t + \phi_r)}$, $\mathbf{E}_t = \mathbf{E}_{0t} e^{i(k_t \cdot r - \omega_t t + \phi_t)}$, where $\phi_r$ and $\phi_t$ denote phase
shifts. The $\mathbf{B}$ fields are related to $\mathbf{E}$ by $n \hat{k} \times \mathbf{E} = \mathbf{B}$. To satisfy the boundary conditions, $\theta_i = \theta_r$ and $n_i \sin \theta_i = n_r \sin \theta_r$. The latter is Snell’s law.

In the case of s-polarized light depicted by Figure C-1(A), the two boundary conditions give

$$E_{0i} + E_{0r} = E_{0t}, \quad (C-3)$$

$$\frac{n_i}{\mu_i} (E_{0i} - E_{0r}) \cos \theta_i = \frac{n_t}{\mu_t} E_{0t} \cos \theta_t. \quad (C-4)$$

The amplitude reflection coefficient and amplitude transmission coefficient are solved as

$$r_\perp = \frac{E_{0r}}{E_{0i}} = \frac{\frac{n_t}{\mu_t} \cos \theta_t - \frac{n_i}{\mu_i} \cos \theta_i}{\frac{n_t}{\mu_t} \cos \theta_t + \frac{n_i}{\mu_i} \cos \theta_i}, \quad (C-5)$$

$$t_\perp = \frac{E_{0t}}{E_{0i}} = \frac{2 \frac{n_t}{\mu_t} \cos \theta_t}{\frac{n_t}{\mu_t} \cos \theta_t + \frac{n_i}{\mu_i} \cos \theta_i}. \quad (C-6)$$

Similarly, in the case of p-polarized light depicted by Figure C-1(B),

$$(E_{0i} - E_{0r}) \cos \theta_i = E_{0t} \cos \theta_t, \quad (C-7)$$

$$\frac{n_i}{\mu_i} (E_{0i} + E_{0r}) = \frac{n_t}{\mu_t} E_{0t}. \quad (C-8)$$
which give the amplitude coefficients

\[ r_\parallel = \frac{n_i \cos \theta_i - n_t \cos \theta_t}{n_i \cos \theta_i + n_t \cos \theta_t}, \]
\[ (C-9) \]
\[ t_\parallel = \frac{2 n_i \cos \theta_i}{n_i \cos \theta_i + n_t \cos \theta_t}. \]
\[ (C-10) \]

By considering the product of the intensity and the cross-sectional area of the beams, the reflectance and transmittance are respectively

\[ R = \frac{I_r A \cos \theta_r}{I_i A \cos \theta_i} = |r|^2, \]
\[ (C-11) \]
\[ T = \frac{I_t A \cos \theta_t}{I_i A \cos \theta_i} = \frac{n_t \cos \theta_t |t|^2}{n_i \cos \theta_i}, \]
\[ (C-12) \]
valid for both polarizations. The intensity is the time-averaged magnitude of the Poynting vector \( I = \langle S \rangle = n c \epsilon_0 E^2 / 2 \). \( A \) is the area of the beam on the interface, which cancels out in the calculations.

When dealing with non-magnetic materials, we can take \( \mu_i = \mu_t = 1 \). We will use this assumption in the next section. Under this condition, the reflectance and transmittance for the case of normal incidence can be derived for either the s-polarized or the p-polarized incident light,

\[ R = \left( \frac{n_i - n_t}{n_i + n_t} \right)^2, \]
\[ (C-13) \]
\[ T = \frac{4n_i n_t}{(n_i + n_t)^2}. \]
\[ (C-14) \]

**C.2 Fresnel Equations for Thin Film on Thick Substrate**

Now we consider a beam comes in a medium with refractive index \( n_i \), and incidents on a thin film deposited on a substrate with refractive index \( n_t \). The film thickness is \( d \) and is characterized by its optical conductivity \( \sigma \). We want to calculate the reflectance from the thin film and the transmittance through the thin film into the substrate.
The boundary conditions need to be re-evaluated. Since free charges can be present at the interface due to the thin film, Eq. (C–2) is now different,

\[ \nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{J}_f = \frac{4\pi}{c} \sigma \mathbf{E}_t. \] (C–15)

We have assumed that the electric field is the same in the thin film and just after it enters the substrate, since the thin film is extremely thin compared to the wavelength.

For s-polarized light, the two boundary conditions yield

\[ E_{0i} + E_{0r} = E_{0t}, \] (C–16)
\[ H_{0i} \cos \theta_i - H_{0r} \cos \theta_r - H_{0t} \cos \theta_t = \frac{4\pi}{c} \sigma d E_{0t}. \] (C–17)

The second equation is obtained by integrating Eq. (C–15). Using \( H = nE \), the solutions are

\[ r_{\perp} = \frac{n_t \cos \theta_t - n_i \cos \theta_i + \frac{2\pi}{c} \sigma d}{n_t \cos \theta_t + n_i \cos \theta_i + \frac{4\pi}{c} \sigma d}, \] (C–18)
\[ t_{\perp} = \frac{2n_t \cos \theta_t}{n_t \cos \theta_t + n_i \cos \theta_i + \frac{4\pi}{c} \sigma d}. \] (C–19)
For the case of p-polarization, we have

\[
(E_0i - E_{0r}) \cos \theta_i = E_{0t} \cos \theta_t, \tag{C-20}
\]
\[
n_i(E_{0i} + E_{0r}) - n_t E_{0t} = \frac{4\pi}{c} \sigma d E_{0t} \cos \theta_t. \tag{C-21}
\]

The solutions are

\[
r_\parallel = \frac{n_t \cos \theta_i - n_i \cos \theta_t + \frac{4\pi}{c} \sigma d \cos \theta_i \cos \theta_t}{n_t \cos \theta_i + n_i \cos \theta_t + \frac{4\pi}{c} \sigma d \cos \theta_i \cos \theta_t}, \tag{C-22}
\]
\[
t_\parallel = \frac{2n_i \cos \theta_i}{n_t \cos \theta_i + n_i \cos \theta_t + \frac{4\pi}{c} \sigma d \cos \theta_i \cos \theta_t}. \tag{C-23}
\]

In the above equations, we can write \(4\frac{(\pi/c)\sigma d}{Z_0/R_\square}\) as \(Z_0/R_\square\), where \(Z_0 = 4\pi/c \approx 377 \, \Omega/\square\) is the vacuum impedance and \(R_\square = 1/\sigma d\) is the thin film impedance.

Consider a specific case in which light is incident from vacuum on a thin film with \(\sigma = \sigma_1 + i\sigma_2\) and thickness \(d\). The substrate has refractive index \(n\). For p-polarized incident waves, for instance, the reflectance and transmittance are

\[
R_\parallel = \frac{(n - \frac{\cos \theta_i}{\cos \theta_t} + Z_0\sigma_1 d \cos \theta_i)^2 + (Z_0\sigma_2 d \cos \theta_i)^2}{(n + \frac{\cos \theta_i}{\cos \theta_t} + Z_0\sigma_1 d \cos \theta_i)^2 + (Z_0\sigma_2 d \cos \theta_i)^2}, \tag{C-24}
\]
\[
T_\parallel = \frac{4n \frac{\cos \theta_i}{\cos \theta_t}}{(n + \frac{\cos \theta_i}{\cos \theta_t} + Z_0\sigma_1 d \cos \theta_i)^2 + (Z_0\sigma_2 d \cos \theta_i)^2}. \tag{C-25}
\]

For the case of normal incidence, \(\theta_i = \theta_t = 0\). Suppose light is incident from vacuum to a thin film on a substrate with refractive index \(n\). These equations reduce to the well-known equations derived by Tinkham and Palmer [38],

\[
r_f = \frac{n - 1 + Z_0\sigma d}{n + 1 + Z_0\sigma d}, \tag{C-26}
\]
\[
t_f = \frac{2}{n + 1 + Z_0\sigma d}, \tag{C-27}
\]
\[
R_f = \frac{(n - 1 + Z_0\sigma_1 d)^2 + (Z_0\sigma_2 d)^2}{(n + 1 + Z_0\sigma_1 d)^2 + (Z_0\sigma_2 d)^2}, \tag{C-28}
\]
\[
T_f = \frac{4n}{(n + 1 + Z_0\sigma_1 d)^2 + (Z_0\sigma_2 d)^2}. \tag{C-29}
\]
We have dropped the polarization symbol because s and p polarizations are indistinguishable at normal incidence. Instead we put an $f$ as the subscript, meaning transmittance across and reflectance from the thin film. The observed reflectance and transmittance are usually different from $R_f$ and $T_f$ because substrates are involved.

**C.3 External Reflectance and Transmittance for Thin Film on Thick Substrate**

In Section C.2 we have derived the reflectance from the thin film and also the transmittance into the substrate, without consideration of the interference effects in the substrate. Practically it has to be taken into account, because the quantities measured are the external reflection and transmission determined by both the thin film and the substrate.

**C.3.1 Method of Summation**

Consider the configuration shown in Figure C-3. It is similar to the problem of finding the reflectance and transmittance of a Fabry-Pérot interferometer [171], the difference being the presence of the thin film in between Medium 1 and Medium 2. A thin film of thickness $d$, deposited on a substrate of thickness $d_s$ and refractive index $n_2$, is sandwiched between two media of refractive indices $n_1$ and $n_3$. In our experiment they are vacuum, so we take $n_1 = n_3 = 1$. We write $n_2 = n$ for simplicity. We consider the general case when absorption is present in the substrate, described by the extinction coefficient $\kappa$ or the absorption coefficient $\alpha = 2\omega\kappa/c$. The amplitude reflection coefficient between Medium 1 and Medium 2 is $r_f$ and the amplitude transmission coefficient is $t_f$. Depending on the polarization they are given either by Eqs. (C-18) and (C-19) or Eqs. (C-22) and (C-23). The amplitude reflection and transmission coefficients for light propagating from Medium 2 to Medium 1 are denoted as $r'_f$ and $t'_f$, respectively. They can be evaluated by simply swapping the refractive indices $n_i$ and $n_t$ in Eqs. (C-18), (C-19), (C-22), and (C-23). The amplitude reflection coefficient between Medium 2 and Medium 3 is denoted as $r_{23}$,
and $t_{23}$ for transmission. By tracing the beam, we can determine the amplitude of each wave. The first few are labeled in Figure C-3.

The resultant amplitude transmission and reflection coefficients are the summation of all the transmission and reflection amplitudes. However all beams should be measured along a line perpendicular to the direction of final propagation. Take the first two reflected beams for example. The second reflected beam travels $r_2 = 2d_s / \cos \theta_2$ in Medium 2, but is then retarded from the first reflected beam by a distance $r_1 = 2d \tan \theta_2 \sin \theta_1$ in Medium 1. Assume all waves treated here are planes waves of the form $E = E_0 e^{i(kr-\omega t)}$. The phase factor of the second reflected beam differs from that of the first reflected beam by an amount

$$e^{kr_2} \cdot e^{-k_1 r_1} = e^{i\frac{\omega}{c}(n_2 + i\kappa_2)2d_s / \cos \theta_2}, e^{-i\frac{\omega}{c}n_1 2d_s \tan \theta_2 \sin \theta_1}$$

$$= e^{-2\omega \kappa_2 d_s / \cos \theta_2}, e^{i\frac{\omega}{c}(2n_2 2d_s / \cos \theta_2 - 2n_1 d_s \tan \theta_2 \sin \theta_1)}$$

$$= e^{-\alpha d_s / \cos \theta_2}, e^{i\frac{\omega}{c}2n_2 d_s \cos \theta_2},$$

where $\alpha = 2\omega \kappa_2 / c = 2\omega \kappa / c$ is the absorption coefficient of the substrate, i.e., Medium 2. In getting the second exponential term we used Snell’s law, $n_1 \sin \theta_1 = n_2 \sin \theta_2$. To

\[ \text{(C-30)} \]
simplify the notation, we denote \( d_s / \cos \theta_2 \) as \( x \) and \( (\omega / c)2n_2d_s \cos \theta_2 \) as \( \delta \),

\[
\delta = \frac{\omega}{c}2n_2d_s \cos \theta_2 = (4\pi nd_s \cos \theta_2)\nu. \tag{C-31}
\]

The above exponential factor becomes \( e^{-\alpha \delta}e^{i\delta} \).

Up to a constant phase factor, the total amplitude reflection coefficient is

\[
r = r_f + t_f r_{23} t_f' e^{-\alpha \delta} + t_f r_{23}^2 t_f' t_f e^{-2\alpha \delta} e^{i2\delta} + t_f r_{23}^3 t_f' t_f^2 e^{-4\alpha \delta} e^{i4\delta} + \ldots
\]

\[
= r_f + r_{23} t_f t_f' e^{-\alpha \delta} [1 + r_{23} r_f' e^{-\alpha \delta} + r_{23}^2 r_f' e^{-2\alpha \delta} + \ldots]
\]

\[
= r_f + \frac{r_{23} t_f t_f' e^{-\alpha \delta}}{1 - r_{23} r_f' e^{-\alpha \delta}}, \tag{C-32}
\]

and the total amplitude transmission coefficient is

\[
t = t_f t_{23} e^{-\alpha \delta / 2} + t_f r_{23} t_f' t_{23} e^{-3\alpha \delta / 2} e^{i \delta} + t_f r_{23}^2 t_f' t_{23} e^{-5\alpha \delta / 2} e^{i2 \delta} + \ldots
\]

\[
= t_f t_{23} e^{-\alpha \delta / 2} \left[ 1 + r_{23} r_f' e^{-\alpha \delta} + r_{23}^2 r_f' e^{-2\alpha \delta} + \ldots \right]
\]

\[
= \frac{t_f t_{23} e^{-\alpha \delta / 2}}{1 - r_{23} r_f' e^{-\alpha \delta}}. \tag{C-33}
\]

The reflectance and transmittance are

\[
R = |r|^2 = r_f^2 + \frac{r_{23}^2 t_f t_f' e^{-2\alpha \delta}}{1 + r_{23}^2 r_f^2 e^{-2\alpha \delta} - 2r_{23} r_f' e^{-\alpha \delta} \cos \delta}
\]

\[
+ 2r_f r_{23} t_f t_f' e^{-\alpha \delta} \frac{\cos \delta - r_{23} r_f' e^{-\alpha \delta}}{1 + r_{23}^2 r_f^2 e^{-2\alpha \delta} - 2r_{23} r_f' e^{-\alpha \delta} \cos \delta}, \tag{C-34}
\]

\[
T = \frac{n_3 \cos \theta_3}{n_1 \cos \theta_1} |t|^2 = |t|^2 = \frac{t_f^2 t_{23}^2 e^{-\alpha \delta}}{1 + r_{23}^2 r_f^2 e^{-2\alpha \delta} - 2r_{23} r_f' e^{-\alpha \delta} \cos \delta}. \tag{C-35}
\]

In these equations, \( r_f \) is given by Eq. (C-18) or Eq. (C-22), \( t_f \) is given by Eq. (C-19) or Eq. (C-23), \( r_{23} \) is given by Eq. (C-5) or Eq. (C-9), \( t_{23} \) is given by Eq. (C-6) or Eq. (C-10), \( r_f' \) and \( t_f' \) are obtained from Eq. (C-18) and Eq. (C-19) or Eq. (C-22) and Eq. (C-23) by swapping the refractive index of the substrate and vacuum.

The cosine term describes the oscillatory fringes in the spectrum due to the coherent multiple internal reflections in the substrate. If the measurement resolution is so low that
the fringes are not resolved, incoherent spectra are obtained. These can be calculated from Eqs. (C–34) and (C–35) by averaging the spectra over the cycles of the fringes, noting that the Fresnel coefficients are slowly varying in frequency and can be treated as constant in the cycles used in the averaging. Averaging over a half of the fringe period

$$T = \frac{2\pi}{4\pi nd_s \cos \theta_2} = \frac{1}{2nd_s \cos \theta_2}$$  \hspace{1cm} (C–36)

is sufficient. Making use of the following integration result,

$$\int \frac{dx}{a + b \cos (mx)} = -\frac{1}{m} \frac{1}{\sqrt{a^2 - b^2}} \arcsin \left[ \frac{a \cos (mx) + b}{b \cos (mx) + a} \right] \hspace{1cm} (a^2 > b^2),$$  \hspace{1cm} (C–37)

one finds

$$\frac{1}{T/2} \int_0^{T/2} \frac{d\nu'}{1 + r_{23}^2 \rho_f^2 e^{-2\alpha x} - 2r_{23} \rho_f e^{-\alpha x} \cos (2\pi \nu' / T)} = \frac{1}{1 - r_{23}^2 \rho_f^2 e^{-2\alpha x}}.$$  \hspace{1cm} (C–38)

The incoherent reflectance and transmittance are

$$R_{\text{incoherent}} = \frac{1}{T/2} \int_0^{T/2} R [\cos (2\pi \nu' / T)] \, d\nu' = r_f^2 + \frac{r_{23}^2 \rho_f^2 \rho_{f'}^2 e^{-2\alpha x}}{1 - r_{23}^2 \rho_f^2 e^{-2\alpha x}},$$  \hspace{1cm} (C–39)

$$T_{\text{incoherent}} = \frac{1}{T/2} \int_0^{T/2} T [\cos (2\pi \nu' / T)] \, d\nu' = \frac{\rho_f^2 \rho_{f'}^2 e^{-\alpha x}}{1 - r_{23}^2 \rho_f^2 e^{-2\alpha x}}.$$  \hspace{1cm} (C–40)

For normal incidence, $R_f = r_f^2$ given by Eq. (C–28), $R_{23} = r_{23}^2 = (n - 1)^2 / (n + 1)^2$, $T_{23} = (n_3 \cos \theta_3 / n_2 \cos \theta_2) t_{23}^2 = t_{23}^2 / n = 1 - R_{23}$, $T_f = (n_2 \cos \theta_2 / n_1 \cos \theta_1) t_f^2 = n t_f^2$, $t' = n t_f$, and

$$R' = r_f' = (1 - n + Z_0 \sigma_1 d)^2 + (Z_0 \sigma_2 d)^2 \div (1 + n + Z_0 \sigma_1 d)^2 + (Z_0 \sigma_2 d)^2.$$  \hspace{1cm} (C–41)

The incoherent reflectance and transmittance are

$$R_{\text{incoherent,normal}} = R_f + \frac{R_{23} T_f^2 e^{-2\alpha x}}{1 - R_{23} R_f' e^{-2\alpha x}},$$  \hspace{1cm} (C–42)

$$T_{\text{incoherent,normal}} = T_f \frac{(1 - R_{23}) e^{-\alpha x}}{1 - R_{23} R_f' e^{-2\alpha x}}.$$  \hspace{1cm} (C–43)
C.3.2 Matrix Method

Another approach of solving this problem is the matrix method. It provides a general procedure for treating stratified medium whose properties are constant throughout each plane perpendicular to a fixed direction. Multilayer systems belongs to this category.

Consider a multilayer system with \( m \) layers sandwiched between the first layer denoted as \( f \) and the last layer denoted as \( l \). Each layer is homogeneous and is characterized by it complex refractive index \( N_j \) and thickness \( h_j \). Light propagates from Layer \( f \) to Layer \( l \). The angle of incidence from Layer \( j - 1 \) to Layer \( j \) is \( \theta_j \). We would like to calculate the transmittance to Layer \( l \) and reflectance to Layer \( f \).

The characteristic matrix that relates the electromagnetic waves entering and exiting the \( j \)th layer is

\[
M_j = \begin{bmatrix}
\cos (2\pi \nu N_j h_j \cos \theta_j) & -i p_j \sin (2\pi \nu N_j h_j \cos \theta_j) \\
-ip_j \sin (2\pi \nu N_j h_j \cos \theta_j) & \cos (2\pi \nu N_j h_j \cos \theta_j)
\end{bmatrix},
\]

(C–44)

where \( p_j = N_j \cos \theta_j \) for s-polarized light and \( p_j = \cos \theta_j/N_j \) for p-polarized light. The amplitude reflection and transmission coefficients are

\[
r = \frac{(m_{11} + m_{12} p_f) p_f - (m_{21} + m_{22} p_l)}{(m_{11} + m_{12} p_f) p_f + (m_{21} + m_{22} p_l)},
\]

(C–45)

\[
t = \frac{2p_f}{(m_{11} + m_{12} p_f) p_f + (m_{21} + m_{22} p_l)},
\]

(C–46)

where \( m_{11}, m_{12}, m_{21}, \) and \( m_{22} \) are the components of the following matrix,

\[
M = M_1 M_2 \cdots M_m = \begin{bmatrix}
m_{11} & m_{12} \\
m_{21} & m_{22}
\end{bmatrix}.
\]

(C–47)

\( p_f \) and \( p_l \) are determined by the first and the last layer. The reflectance and transmittance are

\[
R = |r|^2,
\]

(C–48)

\[
T = \frac{p_l}{p_f} |t|^2.
\]

(C–49)
Apply this method to our two-layered system \((m_{\text{total}} = 2)\). The layer \(m = 1\) is the thin film with optical conductivity \(\sigma\) and thickness \(d\). The corresponding complex refractive index can be calculated from \(\sigma\) using Table B-1. The layer \(m = 2\) is the substrate with refractive index \(n_2\) and thickness \(d_s\). Since we are considering the transmission and reflection into vacuum on the two sides of the two-layered system, the first and last layers are vacuum, \(n_f = n_l = 1\) in the calculation of \(p_f\) and \(p_l\). With these conditions the transmittance and reflectance can be readily calculated.

Figure C-4 shows the superconducting-state transmittance of NbTiN on a quartz substrate at 2 K, 0 T, normalized to its normal-state value. The resolution of the measurement is 1 cm\(^{-1}\), which enables us to resolve the multiple internal reflections in the quartz substrate. The smooth curve is the incoherent external transmittance ratio calculated from Eq. (C–43), with \(\sigma_1\) and \(\sigma_2\) form the Mattis-Bardeen theory (left panel of Figure 4-4). The curve with oscillatory features is calculated using the matrix method, with the same \(\sigma_1, \sigma_2\), and the refractive index of quartz. In experiments discussed in Chapter 4 and Chapter 5, we chose a lower resolution, typically 4 cm\(^{-1}\), so that the oscillatory features do not appear in the spectra. This avoids the complications due to the substrate and simplifies the data analysis.
Figure C-4. $\tau_s/\tau_n$ data (circles) of NbTiN at 2 K measured with a resolution of 1 cm$^{-1}$. The smooth curve is a calculation using Eq. (C-43), with $\sigma_1$ and $\sigma_2$ form the Mattis-Bardeen theory. The curve with oscillatory features is calculated using the matrix method with the same $\sigma_1$, $\sigma_2$, and the refractive index of quartz.
APPENDIX D
CORRECTION OF REFLECTION DATA

Before being used for analysis, the reflectance of NbTiN measured using the sample holder shown in the right of Figure 4-1 must be firstly corrected for the stray light and then for the finite angle of incidence. The methods for these two corrections are in this appendix.

D.1 Correction for Stray Light

The stray light consists of two parts, one from the reflection at the brass cone holding the sample (the middle piece shown in the right panel of Figure 4-1) and the other from the reflection at the brass surface just behind the sample. The latter contribution is important because the sample is partially transmissive in our frequency range of interest. To make the correction, we first measured the empty sample holder including the brass piece behind the sample. The spectrum is denoted as $R_e$. We then mounted and measured the spectrum of a piece of black sand paper with a rough surface. The measured spectrum is $R_k$. The third spectrum, denoted as $R'_n$, was measured with the sample mounted. All spectra were taken at room temperature. $R'_n$ is therefore the measured normal-state reflection. The prime symbol is to distinguish it as a directly measured quantity rather than the one we would measure in the absence of the stray light (denoted as $R_n$).

The reflectance of brass is almost temperature independent in the far-infrared. $R_k$ should then be a constant in all measurements. The reflection from the top brass piece (denoted as $R_b$) in the absence of sample is $R_b = R_e - R_k$, which is also independent of temperature. Considering all contributions to the measured quantity,

$$R'_n = R_n + R_k + R_b T_n^2,$$

where $T_n$ is the normal-state transmittance of the sample, calculated from Eq. (4–4).

Similarly the measured superconducting-state reflection is

$$R'_s = R_s + R_k + R_b T_s^2,$$
in which $\mathcal{T}$ is the superconducting-state transmittance derived from the measured ratio $T_s/T_n$ and the calculated $T_n$. From the two equations above we can relate the ratio of actual reflectance $R_s/R_n$ to the ratio of measured reflectance $R'_s/R'_n$, 

$$\frac{R_s}{R_n} = \frac{\frac{R'_s}{R'_n} - \frac{R_k}{R'_n}}{1 - \frac{R_k}{R'_n}} - \left(\frac{\frac{R_s}{R_n} - \frac{R'_s}{R'_n}}{\frac{R'_s}{R'_n}}\right) \mathcal{T}^2_s.$$  

(D–3)

We realized later that the above correction can be simplified if $R'_s$ and $R'_n$ were measured with the sand paper left in between the sample and the brass surface. The contributions from $R_b$ can be neglected in Eqs. (D–1) and (D–2). As a result,

$$\frac{R_s}{R_n} = \frac{\frac{R'_s}{R'_n}}{1 - \frac{R_k}{R'_n}}.$$  

(D–4)

This is used for some of the data measured with the sand paper behind the sample to eliminate the stray light $R_b$.

### D.2 Correction for Finite Angle of Incidence

The correction for angle of incidence can be calculated from the Fresnel equation derived in the Appendix C. The synchrotron radiation is predominantly parallel-polarized with respect to the plane of incidence. For angle of incidence $\theta_i$ and the corresponding angle of refraction $\theta_t$ determined by Snell’s law, the thin film superconducting-state reflectance is given by Eq. (C–24),

$$R_{f,s} = \left(\frac{n - \cos \theta_t \cos \theta_i + \frac{Z_0 \cos \theta_t \sigma_1}{\frac{R_\square}{\sigma_n}}}{n - \cos \theta_t \cos \theta_i + \frac{Z_0 \cos \theta_t \sigma_1}{\frac{R_\square}{\sigma_n}}}\right)^2 + \left(\frac{\frac{Z_0 \cos \theta_t \sigma_2}{\frac{R_\square}{\sigma_n}}}{\frac{Z_0 \cos \theta_t \sigma_2}{\frac{R_\square}{\sigma_n}}}\right)^2.$$  

(D–5)

The normal-state value $R_{f,n}$ can be obtained by setting $\sigma_1 = \sigma_n$ and $\sigma_1 = 0$. Using the approximation discussed in Section 4.4.1, the ratio of the external reflections are

$$\frac{R_s(\theta_i)}{R_n(\theta_i)} \approx \frac{R_{f,s}(\theta_i)}{R_{f,n}(\theta_i)} = \left(\frac{n - \cos \theta_t \cos \theta_i + \frac{Z_0 \cos \theta_t \sigma_1}{\frac{R_\square}{\sigma_n}}}{n - \cos \theta_t \cos \theta_i + \frac{Z_0 \cos \theta_t \sigma_1}{\frac{R_\square}{\sigma_n}}}\right)^2 + \left(\frac{\frac{Z_0 \cos \theta_t \sigma_2}{\frac{R_\square}{\sigma_n}}}{\frac{Z_0 \cos \theta_t \sigma_2}{\frac{R_\square}{\sigma_n}}}\right)^2.$$  

(D–6)
Figure D-1. (a) $\alpha$ at different temperatures calculated for NbTiN. $\sigma_1$ and $\sigma_2$ at different temperatures are calculated from the Mattis-Bardeen theory. (b) Relative change of $\alpha$ at different temperatures compared to that at 2 K, calculated as $1 - \alpha(T)/\alpha(2 \text{ K})$.

The reflection measurements were performed with $\theta_i = 30^\circ$. To convert to normal-incidence reflection, the reflection ratio data should be multiplied by a factor

$$\alpha = \frac{\mathcal{R}_s(0^\circ)/\mathcal{R}_n(0^\circ)}{\mathcal{R}_s(30^\circ)/\mathcal{R}_n(30^\circ)}$$

(D–7)
calculated from Eq. (D–6). However the calculation requires prior knowledge of the superconducting-state optical conductivity, which is the quantity of our objective. We make the assumption that to the first-order approximation we can use the low-temperature (2 K) zero-field optical conductivity calculated from the Mattis-Bardeen theory. At higher temperature, the deviation of this multiplication factor $\alpha$ from its 2-K value is small in the frequency range of interest, shown in Figure D-1. The magnetic-field-induced deviation is expected to be even smaller, as can be seen by comparing the field-dependent transmission and reflection to the temperature-dependent transmission and reflection.

**D.3 Temperature Dependence of the Optical Conductivity for NbTiN**

To verify the method for correcting the reflection data described above, we apply it to study the temperature dependence of the optical conductivity for NbTiN. The result should be consistent with the Mattis-Bardeen theory.
The superconducting-state to normal-state transmission ratio and reflection ratio are shown in Figure D-2 for different temperatures, all measured using the same experimental procedures for the NbTiN sample described in Section 4.3.2. The reflection data are the raw experiment data without any correction. Both the transmission ratio and the reflection ratio indicate the gap reduction as temperature increases, manifested as the peak shift in $T_s/T_n$ and the dip shift in $R_s/R_n$.

Using the method described above in Section D.1 and Section D.2, we corrected for the stray light and the 30° angle of incidence for the reflection data. We then extracted $\sigma_1$ and $\sigma_2$ from the $T_s/T_n$ and $R_s/R_n$ data from Eqs. (4-9) and (4-10), using the method described in Section 4.4.1. The results are shown in Figure D-3. The solid lines in the left panel are fits to the Mattis-Bardeen theory, and those in the right panel are the corresponding $\sigma_2/\sigma_n$ calculated from the theory. We first fitted the 2 K data with the zero-temperature optical gap $2\Delta_0$ as the only fitting parameter. Then we kept this value fixed and varied temperature to fit the data at higher temperatures. The method works well for $\sigma_1$ up to 8 K, but is not reliable for extracting $\sigma_2$. One of the difficulties lies in the fact that the term under the square root in Eq. (4-10) cannot be guaranteed to be positive due to measurement errors in the data. This explains the missing data points.
Figure D-3. Real part (left) and imaginary part (right) of the optical conductivity for NbTiN at different temperatures, normalized to the normal-state value $\sigma_n$. The solid lines in the left panel are fits using the Mattis-Bardeen theory. The solid lines in the right panel are the corresponding calculated imaginary part for $\sigma_2$ at frequencies above 40 cm$^{-1}$ in the right panel of Figure D-3. For the calculated $\sigma_2$ at all temperatures, a strong coupling correction is included. At 10 K the extracted optical conductivity has poor quality, possibly because the error in the angle-of-incidence correction is too significant to be ignored, especially at low frequency near the gap.

We also found that the fitted temperatures for the data above 2 K are consistently 0.1 K-0.6 K higher than the readings recorded from the temperature sensor. This may be because the temperature sensor was not directly attached to the sample, causing a temperature gradient between the sensor and the sample.

Overall, the correction method is reliable for the temperature-dependence study at temperatures not too close to $T_c$. We expect it should work well for the field-dependence study at low temperature.
APPENDIX E
DATA NOT DISCUSSED

This appendix include some data not discussed. For comparison, some data discussed in the main part of the dissertation are also included.

Figure E-1. Temperature dependence of $\frac{T_s}{T_n}$ and $\frac{R_s}{R_n}$ for NbTiN. The normal state is at 20 K. The measurement resolution is 4 cm$^{-1}$. The data at 2 K, 4 K, 6 K, 8 K, and 10 K are discussed in Appendix D.3.

Figure E-2. Temperature dependence of $\frac{T_s}{T_n}$ and $\frac{R_s}{R_n}$ for NbN. The normal state is at 20 K. The measurement resolution is 4 cm$^{-1}$.
Figure E-3. $\tau_s/\tau_n$ of NbTiN with the magnetic field parallel, at a small angle ($\sim5^\circ$), and perpendicular to the film surface. The data in parallel fields and perpendicular fields are discussed in Chapter 4 and Chapter 5, respectively.
Figure E-4. −\(\Delta T/T\) of NbTiN at different fluences, fields, and delay times. The field is parallel to the film. \(\Delta T = T' - T\), where \(T'\) is the transmission at the specified delay time after laser excitation, and \(T\) is the transmission well before the arrival of the laser pulses so that no photo-excitations are present.
REFERENCES


dynamics in high-temperature superconductors: Experiments and theory,” in
Spectroscopy of Superconducting Materials (American Chemical Society, Washington,
DC, 1999) Chap. 16, pp. 230–244.


films for rf applications,” in Proceedings of the Sixth Workshop on RF Superconduc-


[71] T. Shapoval, H. Stopfel, S. Haindl, J. Engelmann, D. S. Inosov, B. Holzapfel,


[75] B. J. Feenstra, F. C. Klaassen, D. van der Marel, Z. H. Barber, R. P. Pinaya, and


[77] M. S. Pambianchi, S. M. Anlage, E. S. Hellman, E. H. Hartford, M. Bruns, and


BIOGRAPHICAL SKETCH

Xiaoxiang Xi was born in Jiangsu Province, China in 1984. He grew up with a great curiosity in science. He attended Nanjing High School in the same town he was raised. In 2003 he attended Nanjing University, majoring in astronomy. In 2005 he visited the Department of Physics at Hong Kong University of Science and Technology as an exchange student, where he first learned about condensed matter physics. After graduating from Nanjing University in 2007 with a Bachelor of Science degree, he began his graduate study at the Department of Physics, University of Florida. He obtained a Master of Science degree in 2009. He joined Dr. David Tanner’s group in 2008, and worked in close collaboration with Dr. G. Lawrence Carr at the National Synchrotron Light Source, Brookhaven National Laboratory on research in the field of conventional and time-resolved spectroscopy of superconductors and semiconducting nano-structures. He was awarded a Doctor of Philosophy degree in December 2011.