Optical Properties of Organic Superconductor
\( \kappa-(\text{BETS})_2\text{FeBr}_4 \)

by

BAOCHANG LIU

B.Sc. (Hons. Phys), Dalian University of Technology, 2002

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in

The Faculty of Mathematics and Sciences

Department of Physics

BROCK UNIVERSITY
December 14, 2007
2007 © BAOCHANG LIU
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the Brock University, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

(Signature) _______________________

Department of Physics
Brock University
St.Catharines, Canada

Date ___________________________
Abstract

$\kappa$-(BETS)$_2$FeBr$_4$ is the first antiferromagnetic organic superconductor with successive antiferromagnetic and superconducting transitions at $T_N=2.5K$ and $T_c=1.1K$ respectively at ambient pressure. Polarized reflectance measurements were performed on three single crystal-samples of this material using a Brüker IFS66V/S Interferometer, and a Bolometer detector or an MCT detector, at seven temperatures between 4K and 300K, in both the far-infrared and mid-infrared frequency range.

After the reflectance results were obtained, the Kramers-Kronig dispersion relation was applied to determine the optical conductivity of $\kappa$-(BETS)$_2$FeBr$_4$ at these seven temperatures. Additionally, the optical conductivity spectra were fitted with a Drude/Lorentz Oscillator model in order to study the evolution of the optical conductivity with temperature along the a-axis and c-axis. The resistivities calculated from the Drude model parameters along the a-axis and c-axis agreed reasonably with previous transport measurements.
Contents

Abstract .................................................. ii

Contents .................................................. iii

List of Tables ........................................... v

List of Figures .......................................... vi

Acknowledgements ....................................... viii

1 Organic Superconductors .............................. 1

1.1 Introduction ......................................... 1

1.2 $\kappa$-(BETS)$_2$FeBr$_4$ ............................... 2

1.2.1 Crystal Structure .................................. 3

1.2.2 Electronic Structure ............................... 5

1.2.3 Electrical Properties of $\kappa$-(BETS)$_2$FeBr$_4$ .. 6

2 Optical Properties of Materials ....................... 9

2.1 Introduction ......................................... 9

2.2 Kramers-Kronig Analysis ............................ 12

2.3 Oscillator fitting for $\epsilon$ ......................... 14

3 FIR and MIR Spectroscopy Studies of $\kappa$-(BETS)$_2$FeBr$_4$ ......... 19
### Contents

3.1 Introduction .................................................. 19
3.2 Experimental Set-Up ........................................ 20
  3.2.1 Polarization Preference Axis of the Light Source and Interferometer . 22
  3.2.2 Characterization of The New Far-Infrared Polarizer .................. 23
  3.2.3 Far-Infrared Reflectance Spectroscopy Measurement and Results . 25
  3.2.4 The Polarized Mid-Infrared Reflectance Spectroscopy Measurement and Results .................................................. 32

4 Experimental Data Analysis and Results .......................... 35
  4.1 Kramers-Kronig Analysis and Optical Conductivity .................. 35
  4.2 Oscillator Mode Fittings ...................................... 42
  4.3 Resistivity of $\kappa$-(BETS)$_2$FeBr$_4$ .......................... 52

5 Conclusions ...................................................... 54

A Resistivity Parameters for Hagen-Rubens Extrapolation ............. 56

B Demonstration of Background Oscillator and Phonon Mode Fitting .... 57

C Background Oscillator and Phonon Parameters ........................ 59

Bibliography ...................................................... 67
## List of Tables

1.1  Overlap Integrals, Mid-Gap Energies, and Bandwidths of the Upper Band. [8]  5

A.1  Resistivity. ................................................................. 56

C.1  Drude and Oscillator Parameters for a-axis. .......................... 59
C.2  Continued Drude and Oscillator Parameters for a-axis. .......... 60
C.3  Phonon parameters for a-axis. ......................................... 61
C.4  Continued Phonon Parameters for a-axis. ............................ 62
C.5  Drude and Oscillator Parameters for c-axis. ........................ 63
C.6  Continued Drude and Oscillator Parameters for c-axis. ........ 64
C.7  Phonon parameters for c-axis. ......................................... 65
C.8  Continued Phonon Parameters for c-axis. ............................ 66
## List of Figures

1.1 Structures of TMTSF and BEDT-TTF molecules ........................................... 2  
1.2 BETS molecule structure .................................................................................. 2  
1.3 Crystal structure of $\kappa$-(BETS)$_2$FeBr$_4$ ................................................. 4  
1.4 Band structure and Fermi surface of $\kappa$-(BETS)$_2$FeBr$_4$ ......................... 5  
1.5 Temperature dependence of the electrical resistivity of $\kappa$-(BETS)$_2$FeBr$_4$ from 0.6-300K .................................................................................................................. 6  
1.6 Temperature dependence of the lattice constants of $\kappa$-(BETS)$_2$FeBr$_4$ ........ 8  

3.1 Photo of samples on left .................................................................................. 21  
3.2 Sketch of the experimental set-up .................................................................... 21  
3.3 Polarization preference axis test results ......................................................... 23  
3.4 Far-Infrared polarizer leakage test results ...................................................... 24  
3.5 Photograph of the Mid-Infrared experiment set-up ......................................... 25  
3.6 Far-Infrared absolute reflectance along the c-axis of sample A ....................... 27  
3.7 Far-Infrared absolute reflectance along the c-axis of sample B ....................... 29  
3.8 Far-Infrared absolute reflectance along the a-axis of sample B ....................... 30  
3.9 Far-Infrared absolute reflectance along the c-axis of sample C at 295K .......... 32  
3.10 Mid-Infrared absolute reflectance along the a-axis of sample B .................... 33  
3.11 Mid-Infrared absolute reflectance along the c-axis of sample C .................... 34  

4.1 Infrared absolute reflectance along the a-axis of $\kappa$-(BETS)$_2$FeBr$_4$ ........ 36
List of Figures

4.2 Infrared absolute reflectance along the c-axis of \( \kappa\)-(BETS)\(_2\)FeBr\(_4\)........... 37
4.3 Optical conductivities of \( \kappa\)-(BETS)\(_2\)FeBr\(_4\)........................................... 39
4.4 Optical conductivities of \( \kappa\)-(BETS)\(_2\)FeBr\(_4\)........................................... 41
4.5 Background optical conductivities along the a-axis.............................. 45
4.6 Background optical conductivities along the c-axis.............................. 47
4.7 Temperature evolution of some phonon parameters along the a-axis of the sample.......................................................... 49
4.8 Temperature evolution of some phonon parameters along the c-axis of the sample.......................................................... 51
4.9 Resistivities of \( \kappa\)-(BETS)\(_2\)FeBr\(_4\)........................................... 53
B.1 Fitting background oscillators and phonons of a-axis......................... 58
B.2 Fitting background oscillators and phonons of c-axis......................... 58
Acknowledgements

I would first like to thank my supervisor Dr. Maureen Reedyk for accepting me as a graduate student, and then has supported and helped me with solving all difficulties throughout the experiments and data analysis courses. I also benefited from her attitude to research and some independent research opportunities, which makes me a more mature graduate student.

I would also like to specially thank Dr. David Crandles and Dr. Sudhakar Rao. Dr. Crandles’ friendly and patient helps have made sure my experiments going very smoothly. Dr. Sudhakar is not only one of my best colleagues, but he is also one of my best friends.

Another special thanks to every faculty member in the physics department, your kindly assistance and advice made my life at Brock more meaningful and fruitful.

I am thankful to all my friends and office mates at Brock, specially Andrew Davis who has helped me lots with both my study and life in St.Catharines. He has always been one best friends whom I can ask help and advice from.

Additionally, I would really appreciate all helps and technical supports from the machine shop.

Finally, the most special warm thank to my mom for everything she has done for me. This work is dedicated to her and to the memory of my father.
Chapter 1

Organic Superconductors

1.1 Introduction

Organic materials normally act as electrical insulators and do not exhibit the properties of metals due to the absence of any unfilled sites in the conduction and valence bands of organic molecules. In 1973, however, the first true organic metal, tetrathiafulvalene-7,7,8,8-tetraeyano-p- quinodimethane(TTF-TCNQ), was formed from the electron donor tetrathiafulvalene and the electron acceptor tetraeyanoquinodimethane. [1] In 1979, the world's first organic superconductor, (TMTSF)2PF6, was synthesized by Danish researcher Klaus Bechgaard of the university of Copenhagen and three French colleagues. [2] In this substance, tetramethyltetraselenafulvalene (TMTSF) served as the electron donor and PF6 as the electron accepting anion.

In 1982, superconductivity was observed by Parkin et al [3] in the sulphurorganic compound (BEDT-TTF)4(ReO4)2. (BEDT-TTF) is the organic molecule bis-ethylene-dithiatetra-thia-fulvalene. Hundreds of organic conductors have been synthesized since then, more than fifty of which are superconductors with superconducting transition temperatures ranging from 1.2K to 12.6K [4]. Most of these superconductors were developed based either on the TMTSF molecule (also called Bechgaard salts) or on the BEDT-TTF organic molecule (also called ET salts) [5]. One significant difference between these two families of organic superconductors is that the TMTSF-based compounds are classified as quasi 1-D charge transfer salts, while the BEDT-TTF-based compounds, on the other hand are classified as
quasi 2-D charge transfer salts. Figure 1.1 shows the structures of the BEDT-TTF molecule and the TMTSF molecule (Me=Methyl).

![TMTSF and BEDT-TTF molecules](image)

Figure 1.1: Structures of TMTSF and BEDT-TTF molecules. [6]

1.2 $\kappa$-(BETS)$_2$FeBr$_4$

One recently synthesized organic superconductor $\kappa$-(BETS)$_2$FeBr$_4$ is an example of a quasi-2D organic superconductor that is based on the BETS organic molecule [BETS= bis(ethylenedithio)tetraselenafulvalene]. [7] The BETS organic molecule is obtained by substituting four sulfur atoms of the TTF core of BEDT-TTF by four selenium atoms. The BETS has a strong tendency to form a stable metallic state down to liquid helium temperature. [7] Figure 1.2 illustrates the structure of the BETS molecule.

![BETS molecule structure](image)

Figure 1.2: BETS molecule structure. [7]
\( \kappa\text{-}(\text{BETS})_2\text{FeBr}_4 \) is recognized as the first antiferromagnetic organic superconductor with successive antiferromagnetic and superconducting transitions at \( T_N=2.5\text{K} \) and \( T_c=1.1\text{K} \), respectively, at ambient pressure. The absolute reflectance and the subsequently derived optical functions of this material have never been reported. Therefore, it is interesting and worthwhile to conduct this investigation. The results can be compared with the optical properties of both 1-D and 2-D organic superconductors, which may demonstrate some differences and/or similarities. In addition, this hybrid salt system consists of both metamagnetism of the magnetic layer and superconductivity of the conduction layer, which makes it a so-called "dual-functional system". This "dual-function" originates from the interplay of the \( \pi \)-conduction electron from the BETS molecule and the d-localized magnetic moment from the Fe\(^{3+} \) ions. This interaction is named the \( \pi\text{-d} \) interaction. The existence of the \( \pi\text{-d} \) interaction in \( \kappa\text{-}(\text{BETS})_2\text{FeBr}_4 \) has been verified by Fujiwara et al. who observed a small resistivity drop at the Neél temperature. [7]

### 1.2.1 Crystal Structure

Figure 1.3 [7] on the next page shows the crystal structure of \( \kappa\text{-}(\text{BETS})_2\text{FeBr}_4 \). The \( \kappa\text{-}(\text{BETS})_2\text{FeBr}_4 \) salt is orthorhombic with crystal parameters:

\[
a = 11.787(6), \quad b = 36.607(9), \quad c = 8.504(5)\text{Å}, \quad V = 3669(2)\text{Å}^3, \quad Z = 8 \text{ at room temperature} [7].
\]

As Figure 1.3 indicates, the BETS dimers form a two-dimensional conduction layer in the ac-plane. The FeBr\(_4^-\) anions are sandwiched by the conduction layers along the b-direction. The \( \kappa\text{-}(\text{BETS})_2\text{FeBr}_4 \) crystal can be prepared electrochemically under a constant current of 0.7 \( \mu \text{A} \) at 40°C in a chlorobenzene-ethanol solution (9:1 Volume/Volume) containing BETS and tetraethylammonium iron (III) tetrabromide for 2-4 weeks. [8]

As illustrated in Figure 1.3, the two dimensional conduction layer is in the ac plane. The a-axis is named as the easy axis for its energetically favorable direction of the spontaneous
Figure 1.3: Crystal structure of $\kappa$-(BETS)$_2$FeBr$_4$. [7]
magnetization in an antiferromagnetic material. The $\kappa$-(BETS)$_2$FeBr$_4$ samples used for this thesis were in the shape of rhombii, with their a-axis along the long diagonal of the rhombus and their c-axis perpendicular to this axis.

1.2.2 Electronic Structure

A tight-binding band structure and Fermi surface has been calculated at room temperature based on the extended Hückel approximation. The results shown in Table 1.1 [8] are overlap integrals ($10^{-3}$Å), mid-gap energies, and the bandwidth of the upper band of the $\kappa$-(BETS)$_2$FeBr$_4$ salt.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>p</th>
<th>q</th>
<th>c</th>
<th>E mid-gap(eV)</th>
<th>bandwidth(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa$-(BETS)$_2$FeBr$_4$</td>
<td>-22.41</td>
<td>77.33</td>
<td>8.11</td>
<td>35.14</td>
<td>0.68</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Table 1.1: Overlap Integrals, Mid-Gap Energies, and Bandwidths of the Upper Band. [8]

Both the band structure and the Fermi surface of $\kappa$-(BETS)$_2$FeBr$_4$ are shown in Figure 1.4. [8]

Figure 1.4: Band structure and Fermi surface of $\kappa$-(BETS)$_2$FeBr$_4$. [8]

As illustrated in Figure 1.4, the band dispersion of $\kappa$-(BETS)$_2$FeBr$_4$ consists of four energy branches. This is related to the fact that there are four donor molecules in one unit
of the donor layer. A mid-gap between the upper two branches and the lower two branches is observed. The energy of this mid-gap is 0.68eV. The cause of this mid-gap is the strong dimerization of the donor molecules, which also results in the effectively half-filled upper band. [8]

The Fermi surface of $\kappa$-(BETS)$_2$FeBr$_4$, as illustrated in Figure 1.4, is a two-dimensional circle closed in the XV boundary. This is the result of space group symmetry. Other similar samples are the isostructural $\kappa$-(BETS)$_2$FeCl$_4$ and $\kappa$-(BETS)$_2$GaCl$_4$ salts, of which the same Fermi surface structures have been investigated and confirmed by Shubnikov-de Haas and de Haas-Van Alphen oscillations. [8]

### 1.2.3 Electrical Properties of $\kappa$-(BETS)$_2$FeBr$_4$

The temperature dependence of the electrical resistivity of $\kappa$-(BETS)$_2$FeBr$_4$ has been studied, and the result is shown in Figure 1.5 [8].

![Temperature dependence of the electrical resistivity of $\kappa$-(BETS)$_2$FeBr$_4$ from 0.6-300K.](image)

**Figure 1.5:** Temperature dependence of the electrical resistivity of $\kappa$-(BETS)$_2$FeBr$_4$ from 0.6-300K. [8]
This figure presents the experimental results measured for the temperature range from 0.6K—300K within the ac plane at zero magnetic field. From Figure 1.5, it can be seen that upon lowering the temperature from 300K that a slow decrease occurs in the resistivity down to about 200K, followed by a quite sharp increase up to a characteristic peak around 60K; eventually the resistivity decreases very rapidly below 60K. Studies have shown the presence of such a characteristic peak in some other κ-type BEDT-TTF superconductors, and that it is a characteristic behavior for strong electron correlation systems that have a strong intradimer interaction. Furthermore, the resistivity peak observed in κ-(BETS)$_2$FeBr$_4$ is related not only to the strong electron correlation but also to some structural transformations. Experiments have demonstrated that there are some structural anomalies within the temperature range of 60K—140K, as shown in Figure 1.6 [8]. In Figure 1.6, filled squares represent the lattice constants measured during the cooling process, while open circles denote the constants measured upon warming.

From Figure 1.6, abrupt changes can be seen in the a-parameter around 60K and 140K. This anomaly will cause some changes in the electronic band structure. In addition, such a change in the lattice parameter might produce changes in phonon structure, which, as will be shown in Chapter 4, can be observed in optical conductivity spectra within the same temperature range.
Figure 1.6: Temperature dependence of the lattice constants of $\kappa$-(BETS)$_2$FeBr$_4$.

Filled squares: cooling process. Opened circles: warming process. [8]
Chapter 2

Optical Properties of Materials

In this Chapter, the optical properties of materials, specifically the dielectric function $\epsilon$, will be introduced. Following this, Kramers-Kronig relations and oscillator fitting for $\epsilon$ that were used to obtain and to further analyze the dielectric function will be discussed.

2.1 Introduction

The dielectric function, one of the most important optical properties of a material, is widely studied for its sensitive dependence on the electronic band structure. The dielectric function of a material is also able to provide information on the optical conductivity of the material. However, because the dielectric function is not typically directly accessible from experiments, optical reflectance spectroscopy is recognized as a useful and effective means to obtain the dielectric function. The relationship between measurable optical properties and the dielectric function is outlined in what follows.

The experimentally measurable quantity is the reflectance $R$, defined as the ratio of the reflected intensity to the incident intensity of light:

$$ R = \frac{E^*(\text{refl}) \times E(\text{refl})}{E^*(\text{inc}) \times E(\text{inc})} = r^* \times r. \quad (2.1) $$

In equation (2.1), $r$ is called the reflectivity coefficient, and is a complex function of the angular frequency $\omega$. The definition of $r(\omega)$ is the ratio of the reflected electric field $E(\text{refl})$ to the incident electric field $E(\text{inc})$ both at the crystal surface. i.e.
\[
    r(\omega) = \frac{E(\text{refl})}{E(\text{inc})} = \rho(\omega) \exp[i\theta(\omega)].
\]

(2.2)

In the above equation, \( \rho(\omega) \) is the amplitude component of the reflectivity coefficient \( r(\omega) \); and \( \theta(\omega) \) is the phase component of the reflectivity coefficient \( r(\omega) \). Hence, one can write

\[
    R = r^*(\omega) \times r(\omega) = \rho^2(\omega).
\]

(2.3)

It is easy to see that the amplitude component \( \rho(\omega) \) of the reflectivity coefficient \( r(\omega) \) can be calculated using equation (2.4)

\[
    \rho(\omega) = \sqrt{R(\omega)}.
\]

(2.4)

On the other hand, the phase component \( \theta(\omega) \) of the reflectivity coefficient \( r(\omega) \) can be obtained via the use of Kramers-Kronig relations. This will be introduced in detail later.

In addition,

\[
    r(\omega) = \frac{n_1(\omega) + in_2(\omega) - 1}{n_1(\omega) + in_2(\omega) + 1},
\]

(2.5)

where \( n_1(\omega) \), \( n_2(\omega) \) are respectively the real and imaginary parts of the complex refractive index \( N(\omega) \), i.e.

\[
    N(\omega) = n_1(\omega) + in_2(\omega).
\]

(2.6)

The function \( n_1(\omega) \) is also known as the normal refractive index; and \( n_2(\omega) \) is called the extinction coefficient.

From equations (2.2), (2.4) and (2.5), one can derive expressions for \( n_1(\omega) \) and \( n_2(\omega) \) in terms of \( R(\omega) \) and \( \theta(\omega) \), which are:

\[
    n_1(\omega) = \frac{1 - R}{1 + R - 2\sqrt{R} \cos \theta},
\]
Therefore, once both $R(\omega)$, obtained from experiments, and $\theta(\omega)$, obtained from Kramers-Kronig analysis, are known, it is possible to calculate $n_1(\omega)$ and $n_2(\omega)$ via equations (2.7). Consequently, the complex refractive index $N(\omega)$ will be known.

The complex dielectric function and conductivity are defined as

$$\epsilon = \epsilon_1 + i\epsilon_2$$

and

$$\sigma = \sigma_1 + i\sigma_2,$$

and a standard result derived from Maxwell’s equations shows [9]

$$N^2 = \epsilon.$$  

Hence, from equations (2.6), (2.8) and (2.10), one can obtain

$$\epsilon_1 = n_1^2 - n_2^2$$

and

$$\epsilon_2 = 2n_1n_2.$$  

Additionally,

$$\epsilon_1 = 1 - \frac{4\pi\sigma_2}{\omega},$$

$$\epsilon_2 = \frac{4\pi\sigma_1}{\omega},$$

where $\sigma_1$ and $\sigma_2$ denote the real and imaginary parts of the optical conductivity respectively. [10]

Therefore, one can calculate $\epsilon_1$, $\epsilon_2$ via equations (2.7) and (2.11) after knowing $R(\omega)$ and $\theta(\omega)$. Then, the optical conductivity $\sigma$ can be obtained using equations (2.12).
2.2 Kramers-Kronig Analysis

According to equations (2.11) and (2.12), both the real part $n_1$ and the imaginary part $n_2$ of the complex refractive index are needed to determine the dielectric function (i.e. $\epsilon_1$ and $\epsilon_2$) and the optical conductivities $\sigma_1$ and $\sigma_2$. Both $n_1$ and $n_2$ can be calculated via equations (2.7) if both the reflectance, $R(\omega)$, obtained directly from the experimental results and the phase shift, $\theta(\omega)$, are known. Kramers-Kronig Analysis is a mathematical process to calculate the phase $\theta(\omega)$ using the experimental result $R(\omega)$.

Kramers-Kronig Analysis is a classic example of dispersion relations following rigorously from the requirement of causality. Causality is understood to imply that there can be no effect before the cause. The usual forms of the Kramers-Kronig dispersion relations for the dielectric function are [11]:

\[
\epsilon_1(\omega) - 1 = \frac{1}{\pi} \varphi \int_{-\infty}^{+\infty} \frac{\epsilon_2(\omega')}{\omega' - \omega} d\omega' = \frac{2}{\pi} \varphi \int_{0}^{+\infty} \frac{\omega' \epsilon_2(\omega')}{(\omega')^2 - \omega^2} d\omega',
\]

and

\[
\epsilon_2(\omega) = -\frac{1}{\pi} \varphi \int_{-\infty}^{+\infty} \frac{[\epsilon_1(\omega') - 1]}{\omega' - \omega} d\omega' = -\frac{2\omega}{\pi} \varphi \int_{0}^{+\infty} \frac{[\epsilon_1(\omega') - 1]}{(\omega')^2 - \omega^2} d\omega',
\]  

(2.13)

where $\varphi$ denotes the principal value of the integral;

with the conditions

\[
\epsilon_1(-\omega') = \epsilon_1(\omega')
\]

and

\[
\epsilon_2(-\omega') = -\epsilon_2(\omega').
\]

(2.14)

However, the more common dispersion relation used to determine $\epsilon_1$ and $\epsilon_2$ is the phase-shift, $\theta(\omega)$, dispersion relation. A brief derivation of this dispersion relation follows:

The reflectivity coefficient $r(\omega)$ is given as equation(2.2)

i.e.

\[
r(\omega) = \rho(\omega) \exp[i\theta(\omega)].
\]

(2.15)
This equation can also be expressed as

\[ \ln r(\omega) = \ln \rho(\omega) + i \theta(\omega). \]  \hspace{1cm} (2.16)

Considering the fact that the reflectance must obey causality, one can write the following dispersion relation [11]

\[ \ln \rho(\omega) = \frac{1}{\pi} \varphi \int_{-\infty}^{+\infty} \frac{\theta(\omega')}{\omega' - \omega} d\omega' \]

and \[ \theta(\omega) = -\frac{1}{\pi} \varphi \int_{-\infty}^{+\infty} \frac{\ln \rho(\omega')}{\omega' - \omega} d\omega'. \]  \hspace{1cm} (2.17)

Since the input and output functions must be real, \( \theta(\omega) \) can be rewritten as

\[ \theta(\omega) = -\frac{2\omega}{\pi} \varphi \int_{0}^{+\infty} \frac{\ln \rho(\omega')}{(\omega')^2 - \omega^2} d\omega'. \]  \hspace{1cm} (2.18)

The singularity at \( \omega' = \omega \) is removed by subtracting

\[ \frac{2\omega}{\pi} \varphi \int_{0}^{+\infty} \frac{\ln \rho(\omega')}{(\omega')^2 - \omega^2} d\omega' = 0. \]  \hspace{1cm} (2.19)

Hence,

\[ \theta(\omega) = \frac{2\omega}{\pi} \int_{0}^{+\infty} \frac{\ln \rho(\omega') - \ln \rho(\omega)}{\omega^2 - (\omega')^2} d\omega'. \]  \hspace{1cm} (2.20)

Because of equation (2.4), i.e. \( \rho(\omega) = \sqrt{R(\omega)} \); equation (2.20) can be rewritten in terms of \( R(\omega) \) as

\[ \theta(\omega) = \frac{\omega}{\pi} \int_{0}^{+\infty} \frac{\ln R(\omega') - \ln R(\omega)}{\omega^2 - (\omega')^2} d\omega'. \]  \hspace{1cm} (2.21)

Therefore, the phase-shift \( \theta(\omega) \) can be obtained numerically via equation (2.21). The \( R(\omega) \) is the reflectance obtained from experiment.
Chapter 2. Optical Properties of Materials

However, since the reflectance can be measured only for a finite frequency range, its extrapolation in regions where data is not available is necessary.

2.3 Oscillator fitting for \( \varepsilon \)

The dielectric function and optical conductivity are often further analyzed using a Drude/Lorentz oscillator model. A typical example of the Lorentz Oscillator Model is an electron of charge \(-e\) and mass \(m\) bound to a nucleus in an atom. The motion of this electron can be described by:

\[
-e \mathbf{E} - m \omega^2 \mathbf{r}(\omega) - m \tau \dot{\mathbf{r}}(\omega) = m \ddot{\mathbf{r}}(\omega),
\]

where \(\mathbf{E}\) is a time dependent electrical field expressed in the form of \(\mathbf{E} = \mathbf{E}_0 \exp(-i \omega t)\), the term \(m \omega^2 \mathbf{r}\) is a Hooke’s law restoring force, and the term \(m \tau \dot{\mathbf{r}}\) represents viscous damping arising from various scattering mechanisms in a solid. \(\tau\) is the scattering rate.

The solution to equation (2.22) is:

\[
\mathbf{r}(\omega) = \frac{-e (\mathbf{E}/m)}{\omega^2 - \omega^2 - i \tau \omega}.
\]

As defined in most introductory texts on electromagnetic theory and solid state physics, [13] the displacement vector is:

\[
\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} = \varepsilon \mathbf{E},
\]

where \(\mathbf{P}\) is the dipole moment per unit volume, and \(\varepsilon\) is the dielectric function of a medium.

Additionally, the dipole moment is:
\[ P = -er. \] (2.25)

Hence, combining equations (2.23), (2.24) and (2.25), plus considering N atoms per unit volume as well, one can derive:

\[ \epsilon = 1 + \frac{4\pi Ne^2}{m} \frac{1}{\omega_0^2 - \omega^2 - i\tau \omega}. \] (2.26)

Usually, the plasma frequency is defined as,

\[ \omega_p^2 = \frac{4\pi Ne^2}{m}. \] (2.27)

If there are more than one bound electron per atom, equation (2.26) can be extended,

\[ \epsilon = 1 + \frac{4\pi e^2}{m} \sum_j \frac{N_j}{\omega_j^2 - \omega^2 - i\tau_j \omega} \]

and \[ \sum_j N_j = N, \] (2.28)

where \( N_j \) is the density of electrons bound with resonance frequency \( \omega_j \) and scattering rate \( \tau_j \).

Similarly, a corresponding quantum mechanical equation can be derived,

\[ \epsilon = 1 + \frac{4\pi e^2}{m} \sum_j \frac{Nf_j}{\omega_j^2 - \omega^2 - i\tau_j \omega}. \] (2.29)

However, in equation (2.29) \( \omega_j \) is the transition frequency of an electron between two atomic states separated in energy by \( h\omega_j \). The parameter \( f_j \) is called the oscillator strength, which is a measure of the relative probability of a quantum mechanical transition. Therefore, it satisfies the so-called f-sum rule, i.e.

\[ \sum_j f_j = 1. \] (2.30)
Chapter 2. Optical Properties of Materials

The Lorentz oscillators are used to model phonons and bound electronic transitions. In a metal, because the free conduction electrons do not experience restoring forces (i.e. \( \omega_0 = 0 \)) the term \( m \omega_r^2 \mathbf{r} \) in equation (2.22) does not appear. And, thus derived in the same manner described above, the dielectric function is written as:

\[
\epsilon = 1 - \frac{4\pi Ne^2}{m} \frac{1}{\omega^2 + i\tau_D \omega}. \tag{2.31}
\]

Since this model is normally referred as to the Drude model, \( \tau_D \) denotes the scattering rate of the free electrons. One also defines the plasma frequency as:

\[
\omega_{pD}^2 = \frac{4\pi Ne^2}{m}. \tag{2.32}
\]

Sometimes, phonons are coupled to electronic excitations. If a phonon of resonance frequency \( \omega' \), mass \( m \) effective charge \( q' \) and scattering rate \( \tau' \) in coordinate frame \( \mathbf{l} \) is coupled to an electron \( \omega_i \) in coordinate frame \( \mathbf{r} \), equation (2.22) can be modified to

\[
g \mathbf{l} - e \mathbf{E} - m \omega_i^2 \mathbf{r} - m \tau_i \dot{\mathbf{r}} = m \ddot{\mathbf{r}}. \tag{2.33}
\]

Similarly, in the \( \mathbf{l} \) coordinates, the equation of motion for this phonon is

\[
g \mathbf{r} - q' \mathbf{E} - m' (\omega')^2 \mathbf{l} - m' \tau' \dot{l} = m' \ddot{l}. \tag{2.34}
\]

Here, \( g \) is known as the coupling constant.

The solutions to equations (2.33) and (2.34) are:

\[
\mathbf{r} = \frac{\frac{2}{m} \mathbf{l} - \frac{e}{m} \mathbf{E}}{\omega_i^2 - \omega^2 - i\omega \tau_i}, \tag{2.35}
\]

\[
\mathbf{l} = \frac{\frac{2}{m} \mathbf{r} + \frac{q'}{m} \mathbf{E}}{(\omega')^2 - \omega^2 - i\omega \tau'}. \tag{2.36}
\]
By substituting equation (2.36) into (2.35) and rearranging the form of the result, one can obtain,

\[
\mathbf{r} [\omega_i^2 - \omega^2 - i\omega \tau_i - \frac{g^2}{mm'} \frac{1}{(\omega')^2 - \omega^2 - i\omega'}] = E \left[ \frac{g q'}{mm'} \frac{1}{(\omega')^2 - \omega^2 - i\omega'} - \frac{e}{m} \right]. \quad (2.37)
\]

Defining

\[
D = \frac{1}{\omega_i^2 - \omega^2 - i\omega \tau_i}
\]

and \( D' = \frac{1}{(\omega')^2 - \omega^2 - i\omega'} \). \quad (2.38)

Equation (2.37) can then be rewritten as:

\[
\mathbf{r} \left[ \frac{1}{D} - \frac{g^2}{mm'} D' \right] = E \left[ \frac{g q'}{mm'} D' - \frac{e}{m} \right]. \quad (2.39)
\]

Now, via a similar derivation to that which leads to equation (2.26), one can obtain,

\[
\epsilon = 1 + \frac{\omega_p^2}{\omega_i^2 - \omega^2 - i\omega \tau_i - \frac{g^2}{mm'} D'} (1 - \frac{q' g}{em} D'). \quad (2.40)
\]

If there are k phonons coupled to the same electron at \( \omega_i \), equation (2.40) can then be extended to:

\[
\epsilon = 1 + \frac{\omega_p^2}{\omega_i^2 - \omega^2 - i\omega \tau_i - \sum_k \frac{g^2_k}{mm_k} D'_k} (1 - \sum_k \frac{g' k g}{em_k} D'_k), \quad (2.41)
\]

where,

\[
D'_k = \frac{1}{(\omega'_k)^2 - \omega^2 - i\omega'_k}. \quad (2.42)
\]
To summarize, if a system has \( j \) bound oscillators of frequency \( \omega_j \), free electrons and \( k \) phonons of frequency \( \omega_k \) coupled to an oscillator at \( \omega_i \), based on equations (2.28), (2.29) and (2.31), one can derive the expression for \( \epsilon \) for this system, which is

\[
\epsilon = 1 - \frac{\omega_{P_D}^2}{\omega^2 + i\tau_D \omega} + \frac{4\pi e^2}{m} \sum_j \frac{N_j}{\omega_j^2 - \omega^2 - i\tau_j \omega} + \frac{\omega_{P_i}^2}{\omega_i^2 - \omega^2 - i\omega \tau_i - \sum_k \frac{g_{kk}^2}{m^2} (1 - \sum_k \frac{q_k g_k}{e m_k} D_k')}
\]

where \( \omega_{P_D} \) and \( D_k' \) are given by equations (2.32) and (2.42) respectively. [12]
Chapter 3

FIR and MIR Spectroscopy Studies of \( \kappa-(\text{BETS})_2\text{FeBr}_4 \)

In this chapter, the experimental method used to obtain the far-infrared and the mid-infrared reflectance spectra of the sample \( \kappa-(\text{BETS})_2\text{FeBr}_4 \) will be introduced. This is followed by a presentation of the experimental results obtained for this thesis work.

3.1 Introduction

The objective of the present experiments is to collect polarized far-infrared (FIR) and mid-infrared (MIR) reflectance spectra of the organic superconductor sample \( \kappa-(\text{BETS})_2\text{FeBr}_4 \) within the temperature range from 4K to 300K (room temperature). The absolute reflectance is obtained from the experimental data and is used to determine the dielectric function of the sample via Kramers-Kronig analysis; the optical conductivity of \( \kappa-(\text{BETS})_2\text{FeBr}_4 \) is then further investigated.

The absolute reflectance \( R \) introduced above is defined as the following:

\[
R = \frac{I_{\text{sample}}(\omega)}{I_{\text{reference}}(\omega)} \times \frac{I_{\text{gold-coated sample}}(\omega)}{I_{\text{reference}}(\omega)} \times R_{\text{gold}}(\omega). \tag{3.1}
\]

In equation (3.1), \( I_{\text{sample}}(\omega) \) is the intensity of the reflected light from a sample as a function of its frequency; \( I_{\text{reference}}(\omega) \) denotes the intensity of the source light from an independent reference path; \( I_{\text{gold-coated sample}}(\omega) \) is the intensity of the reflected light from the
Chapter 3. FIR and MIR Spectroscopy Studies of \( \kappa \)-(BETS)\(_2\)FeBr\(_4\)

gold-coated sample; \( R_{\text{gold}}(\omega) \) is the absolute reflectance ratio of gold, which is known to be 0.985. The purpose of the gold evaporation is to eliminate the effects caused by the surface structure of the sample. Sometimes, the ratio of the intensity of light reflected from a sample over that from the reference path is referred to as the intermediate ratio. i.e.

\[
\text{Intermediate ratio} = \frac{I_{\text{sample}}(\omega)}{I_{\text{reference}}(\omega)}.
\]  

(3.2)

The actual experiments performed for this thesis work measured the intensities of both reflected light from the sample (i.e. \( I_{\text{sample}}(\omega) \)) and light from an independent reference path (i.e. \( I_{\text{reference}}(\omega) \)) at each chosen temperature. After the measurements were repeated several times at all chosen temperatures, gold was evaporated in situ on to the sample. Similarly, the intensities of light reflected from the gold coated sample (i.e. \( I_{\text{gold-coated sample}}(\omega) \)) and from the independent reference path were taken at corresponding temperatures. Then, the intermediate ratios and the absolute reflectance were calculated using the experimental software OPUS. Only the absolute reflectance \( R \) is applied to the Kramers-Kronig relation.

### 3.2 Experimental Set-Up

The original rhombus shaped \( \kappa \)-(BETS)\(_2\)FeBr\(_4\) crystal with approximate size of 2mm \( \times \) 3mm was broken in transport to Brock into three pieces, which made it difficult to achieve a reasonable signal size. Figure 3.1 is a photograph of the three pieces of the sample. In order to maximize the signal size, several strategies were followed. The polarization axis preference of the light source was located and the crystal axis of interest aligned with it. Because the commercial far-infrared and mid-infrared polarizer (Infraspecs model P03) was accidentally broken, a far-infrared polarizer made from Sciencetech polarizer material was characterized in the lab and a new mid-infrared polarizer (Specac KRS-5) was purchased. Eventually, the far-infrared and mid-infrared reflectance spectra were collected and are presented in the
following sections. The sketch in Figure 3.2 shows the main experimental set-up.

Figure 3.1: Photo of samples on left. [13]

Figure 3.2: Sketch of the experimental set-up.
3.2.1 Polarization Preference Axis of the Light Source and Interferometer

A globar is used as the light source for the interferometer for the present experiments. This experimental configuration still has some polarization preference. In other words, along a certain direction perpendicular to the propagation direction of the light, the intensity of light is greater than that along other directions. Therefore, if this preferred polarization direction is located and set parallel to the axis of interest of the sample, the detected signal would be maximized.

To find out the polarization preference axis, a commercial far-infrared polarizer (InfraSpecs model P03) was placed in front of both the sample light path and the reference light path. It is known that the transmission axis of the polarizer is along the horizontal direction when the index number on the polarizer mount is 0°, 180° or 360°. By rotating the polarizer by 10° each time through a full rotation of 360°, the intensities of light reflected from a gold-coated sample that does not have polarization dependence itself and directly from the independent reference path were detected. The result is plotted in Figure 3.3, which shows the intensity of light as a function of polarizer angle with the horizontal. The result clearly illustrates that the maximum intensity appears at 0°, 180° and 360°. So, the intensity of the interferometer optics is the greatest along the horizontal direction. This is thus the preferred direction along which to mount the axis of interest of the samples.
3.2.2 Characterization of The New Far-Infrared Polarizer

A Far-Infrared polarizer made from Sciencetech Polarizer material was characterized in the lab due to the accidental formation of a rip in the original one. The new polarizer consists of an aluminium grid of 4μm spacing photolithographically deposited on a 6μm thick substrate. It was placed on the mount of the torn polarizer in order to rotate the transmission axis of the polarizer. The two steps of the characterization were firstly to identify the transmission axis of the new polarizer, and secondly to perform a leakage test. To locate the transmission axis, the torn far-infrared polarizer with the broken section covered and with the transmission axis along the horizontal direction was placed in series with the new one. Upon rotating the new polarizer, the detected intensity of light will be a function of angle. The maximum intensity occurs when the transmission axis of the new polarizer is parallel to that of the original one. The minimum intensity, which theoretically should be zero, happens when the transmission axis of the new polarizer is perpendicular to that of the torn one. However, due to imperfections of the polarizer grid, leakage of the polarizer might result in a non-zero minimum intensity value.

Once the transmission axis of the new polarizer is found. The leakage test is necessary
to verify the reliable frequency range of the new polarizer. An ideal far-infrared polarizer should respond to the frequency range from 0 to 700 cm\(^{-1}\). The premise of this leakage test is that when two transmission axes of two identical polarizers placed in series are parallel to each other, the intensity of the outcoming light is maximum; on the other hand, when two axes are perpendicular to each other, the intensity is minimum within the responding frequency range, and this minimum value ought to be zero ideally. The ratio of the minimum intensity value over the maximum one is often used to evaluate the leakage of a polarizer, i.e.

\[
\text{Leakage} = \frac{\text{Minimum Intensity from two perpendicular axes}}{\text{Maximum Intensity from two parallel axes}}
\]  

(3.3)

Based on this principle, two identical new polarizers were used to perform the leakage test. The results showed that there is 5% leakage within the frequency range from 200cm\(^{-1}\) to 500cm\(^{-1}\) beyond which it increases significantly. Figure 3.4 shows the experimental result.

![Figure 3.4: Far-Infrared polarizer leakage test results.](image-url)
3.2.3 Far-Infrared Reflectance Spectroscopy Measurement and Results

The experiments were performed via the utilization of a Bruker IFS66V/S Interferometer (20-40000 cm\(^{-1}\)), detectors, polarizers and a Janis Industries ST-400 continuous-flow cryostat. A liquid helium cooled Bolometer detector was used for the far-infrared reflectance experiments because of its working frequency range of 50-700 cm\(^{-1}\); while a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector is used for the mid-infrared. Figure 3.5 is a photograph of the mid-infrared experimental set-up. A commercial mid-infrared polarizer was used for the mid infrared experiments while in the far infrared the polarizer described in the previous section was used.

![Figure 3.5: Photograph of the Mid-Infrared experiment set-up.](image)

The far-infrared reflectance experiments were carried out first on the medium size sample A shown in Figure 3.1. The sample was mounted with the easy axis along the vertical direction which is perpendicular to the polarization preference axis of the light source. The far-infrared polarizer was placed with its transmission axis horizontal. The reflectance spectra were investigated at 7 different temperatures: 4K, 30K, 60K, 80K, 100K, 200K and 295K.
The sample was first cooled down to 4.2K, and then was successively heated up to each target temperature. The initial cooling process is accomplished by continuously flowing liquid helium into the cold finger cryostat; while the heating process is achieved via an additional heater controller. After the spectra at each temperature have been collected, the gold evaporation process is performed. Four loops of gold are fixed on the tungsten filament mounted about 12cm from the sample inside the cryostat during the experimental preparation process. Each loop is made from a 5mm long gold wire with 0.2mm diameter. After 1 A current is passed through the filament for about 10 seconds, the current is increased to and held at 2 A for about 30 seconds. After this, gold will coat the surface of the sample. The success of the evaporation process can be monitored via changes of the pressure inside of the sample chamber. The pressure initially increases, and then drops back down. After the process of gold evaporation, similar reflectance experiments are repeated at each temperature. After all of the gold-coated reflectance spectra are collected, the absolute reflectance ratio can be calculated. Figure 3.6 presents the absolute ratios of the c-axis of the sample A.
Chapter 3. FIR and MIR Spectroscopy Studies of κ-(BETS)₂FeBr₄

Figure 3.6: Far-Infrared absolute reflectance along the c-axis of sample A.

The huge noise spikes near 300 cm⁻¹ are caused by some mechanical vibration. This noise was shifted out of the frequency range of interest via slowing of the scan velocity of the interferometer for the remainder of the experiments carried out. One challenge of this investigation was that a particular sample can not be used more than a few times. The reason for this is that the samples are very thin and fragile and thus their surface is damaged, and small pieces removed, every time gold is peeled off.

Next, the same experiment was conducted on the largest sample (sample B). At this time, both the easy axis (a-axis) and c-axis of the sample were investigated. The experimental results are shown in Figures 3.7(a) and 3.8(a). For this experiment, the reflectance spectra along the a-axis on the bare sample were collected first, then the interferometer was opened to adjust the polarizer in order to perform the complete experiment on the c-axis, and then, the polarizer was adjusted again to measure the a-axis on the gold-coated sample. Consequently,
the vacuum condition inside the interferometer and the polarization direction might not be exactly the same for the two measurements on the a-axis before and after gold evaporation. This is likely the cause of the strong interference fringes which did not cancel entirely in the a-axis results. For this reason the a-axis experiment was repeated with sample B without the polarizer and interferometer vacuum being altered throughout the experiment. The results are shown in Figure 3.8(b). Upon comparing Figure 3.6 and 3.7(a) for the c-axis we note in Figure 3.7(a) some additional modes near 400 cm\(^{-1}\) which are absent in Figure 3.6. To investigate this discrepancy further, the c-axis experiment was repeated a third time, and the results are presented in Figure 3.7(b). In Figure 3.7(a) and (b) and 3.6 the features near 250 cm\(^{-1}\) which occur in all c-axis spectra correspond to some phonon modes which will be discussed further when the optical conductivity spectra are introduced.
Figure 3.7: **Far-Infrared absolute reflectance along the c-axis of sample B.** (a): The first set of FIR experimental results obtained along the c-axis at 7 temperatures. (b): The repeated FIR experimental results for the absolute reflectance along the c-axis.
Figure 3.8: Far-Infrared absolute reflectance along the a-axis of sample B. (a): The first set of FIR experimental results obtained along the a-axis at 7 temperatures. (b): The repeated FIR experimental results for the absolute reflectance along the a-axis.
As described in the discussion of Fig 1.5, the resistivity reaches its maximum at 60K, and then dramatically drops down as the temperature decreases further. Since generally for metallic samples higher resistivity corresponds to a lower far-infrared reflectance, the temperature dependence of the reflectance spectra might also be expected to have a minimum reflectance level at 60K which would then increase as the temperature decreases further. This behavior can be seen in most of the experimental results. In Figures (3.6), (3.7) and (3.8), the reflectance at 4K is the highest, and gradually shifts down to its lowest level at the temperature 60K, and then goes up again at 150K and at 295K. The 295K spectra were taken after the sample has been at the room temperature (295K) for a long time (usually at least one night). Hence, for most cases, both the structure and the absolute level of the spectra at 295K are considered highly reliable and reproducible, with the exception of the results of Figure 3.7(a) due to its unreliable experimental method as described above.

Another characteristic of the spectra is the appearance of several peaks occurring near 250 wavenumber at certain temperatures. In Figure 3.6, the three peaks are at 60K, 80K and 100K. In Figures 3.7 and 3.8, the three peaks occur at 45K, 60K and 150K. The appearance of these peaks might be explained as the vibration of the lattice resulting in excited phonon modes. In fact, previous studies have demonstrated some structural anomalies in the same temperature range of 60K-140K. Specifically, the temperature-dependent changes in the a and b lattice parameters are clearly seen in Figure 1.6. Note as well, the dips in both the 4K and the 25K c-axis spectra between 200 and 250 wavenumbers.

In Figure 3.7(a), the two peaks near 400cm$^{-1}$ appear only the first time sample B is measured at 150K and 295K. The appearance of these two modes may have been due to a surface impurity since they did not appear in Figure 3.7(b) nor did they appear in another experiment conducted on sample C at 295K, whose result is shown in Figure 3.9. This latter experiment was carried out to rule out the modes disappearance as a result of surface degradation due to repeated measurements on the same sample.
Chapter 3. FIR and MIR Spectroscopy Studies of κ-(BETS)$_2$FeBr$_4$ 32

3.2.4 The Polarized Mid-Infrared Reflectance Spectroscopy Measurement and Results

Polarized Mid-Infrared reflectance spectra were measured on both the a-axis and c-axis of κ-(BETS)$_2$FeBr$_4$ using essentially the same approach as taken for the Far-Infrared reflectance spectra introduced in the previous sections. However, there were of course a few modifications to the experimental equipment. These modifications include using a Mercury Cadmium Telluride (MCT) detector to replace the Bolometer, and using a commercial mid-infrared polarizer (Specac KRS-5) to replace the far-infrared polarizer. As well, the 6μm Ge-coated Mylar Beamsplitter and the Polypropylene window used for the far-infrared experiments were replaced with a KBr Beamsplitter and a KBr window.

The first experimental attempt was successfully performed on the largest sample (sample B). At this time, the a-axis of sample B was measured, and the results are shown in Figure 3.10.
Figure 3.10: **Mid-Infrared absolute reflectance along the a-axis of sample B.**

The next experiment was carried out on the c-axis of the last piece of sample (sample C) due to the fact that the surface of sample B had become damaged after several repeated experiments. Unfortunately, the measurements could not be accomplished at all seven temperatures because of the formation of a vacuum leak in the MCT detector during the experiment. The surface of sample C was not good enough for another repeated experiment after peeling off the gold. The results shown in Figure 3.11 thus include the spectra at the four temperatures measured.

Although all means of optimization of the signal size were attempted, because of the small size of the samples, the mid-infrared reflectance spectra cut off at a lower frequency than it would be expected.
Figure 3.11: Mid-Infrared absolute reflectance along the c-axis of sample C.
Chapter 4

Experimental Data Analysis and Results

In this chapter, the Kramers-Kronig analysis process is applied to the absolute reflectance to obtain both the dielectric function and the optical conductivity of $\kappa$-(BETS)$_2$FeBr$_4$, and the results are presented. In addition, the results of oscillator fitting to the optical conductivity and of an investigation of the resistivity derived from the optical analysis will be discussed.

4.1 Kramers-Kronig Analysis and Optical Conductivity

As introduced in the previous sections, the optical conductivity of $\kappa$-(BETS)$_2$FeBr$_4$ can be calculated via Kramers-Kronig Analysis (KK analysis) once the infrared reflectance spectra are known. This calculation can be done using SPECAL a well established computer program in the lab. KK analysis requires the reflectance to be known over a frequency range from 0 cm$^{-1}$ to infinity, however, for this thesis work, the reliable experimental results are from 50 cm$^{-1}$ to 2500 cm$^{-1}$ or so. Therefore, in order to apply KK analysis, some experimental data (specifically the absent data below 10000 cm$^{-1}$) were taken from measurements made by Dr. Makariy Tanatar using an infrared microscope, and some extrapolations to both low frequency (below 50 cm$^{-1}$) and high frequency (beyond 10000 cm$^{-1}$) were necessary. For
the extrapolation below 50 cm\(^{-1}\), the Hagen-Rubens relation was applied, and the resistivity parameters used are presented in Appendix A. Beyond 10000 cm\(^{-1}\), the reflectance spectra were extrapolated as a constant up to 300000 cm\(^{-1}\), above which an \(\omega^{-4}\)-relation was employed. This approach is consistent with that taken for \(\kappa-(BEDT-TTF)_2Cu(NCS)_2\) which has a similar Fermi Surface. [14]

Figures 4.1 and 4.2 show the combined far-infrared and mid-infrared experimental reflectance spectra along the a-axis and the c-axis respectively used for KK analysis. Specifically, the far-infrared reflectance results shown in Figure 3.8(b) and the mid-infrared ones shown in Figure 3.10 contributed to Figure 4.1; the far-infrared reflectance results at 4K, 25K, 35K and 295K from Figure 3.7(b) and the mid-infrared ones from Figure 3.11 were used to plot Figure 4.2(a); the far-infrared reflectance results at 45K, 60K and 150K from Figure 3.7(b) and the mid-infrared experimental results from Dr. Tanatar were used to plot Figure 4.2(b) in which the data from Dr. Tanatar is used above 597 cm\(^{-1}\).

Figure 4.1: Infrared absolute reflectance along the a-axis of \(\kappa-(BETS)_2FeBr_4\).
Figure 4.2: Infrared absolute reflectance along the c-axis of \( \kappa-(\text{BETS})_2\text{FeBr}_4 \). (a): Combination of experimental results at 4 temperatures shown in Figures 3.7(b) and 3.11. (b): Combination of experimental results at 3 temperatures shown in Figure 3.7(b) and data from Dr. Tanatar.
From these combined results, the data collected by Dr. Tanatar, and the extrapolation mentioned previously, optical conductivities of \( \kappa-(\text{BETS})_2\text{FeBr}_4 \) along the a-axis and the c-axis at 7 different temperatures were calculated and are shown in Figures 4.3 and 4.4 respectively. Figure 4.3 shows the calculated optical conductivity over the entire experimentally measured range at a few selected temperatures. The focus will be, however, on the results over the frequency range below 4000 cm\(^{-1} \), which are presented in Figure 4.4. Figure 4.4(a) and 4.4(b) show the Kramers-Kronig derived optical conductivity of \( \kappa-(\text{BETS})_2\text{FeBr}_4 \) along the a-axis and c-axis respectively. Note along both axes that at the lowest temperature one observes clear evidence of a Drude-like absorption at the lowest frequencies.
Figure 4.3: **Optical conductivities of \( \kappa-(\text{BETS})_2\text{FeBr}_4 \).** Optical conductivity calculation results along the a-axis (a) and the c-axis (b) respectively within frequency range of 0-10000 cm\(^{-1}\) at 3 temperatures.
Chapter 4. Experimental Data Analysis and Results

Optical conductivity \[1/(\text{Ohm cm})\]

- **295K**:
- **150K**:
- **60K**:
- **45K**:
- **35K**:
- **25K**:
- **4K**:

Frequency \[1/\text{cm}\]
Figure 4.4: Optical conductivities $\sigma_1$ of $\kappa$-(BETS)$_2$FeBr$_4$. The $\sigma_1$ calculation results respectively along the a-axis (a) and the c-axis (b) at 7 temperatures.
4.2 Oscillator Mode Fittings

In order to better investigate and interpret the optical conductivities along the a-axis and c-axis of $\kappa$-(BETS)$_2$FeBr$_4$, the Lorentz-Drude Oscillator model was used to fit the background and phonon modes of the conductivities presented in Figure 4.4. The parameters are tabulated in Appendix C. After this, the fitted phonon modes in the optical conductivity spectra were subtracted from the Kramers-Kronig derived optical conductivity spectra for each axis. Consequently, the temperature evolution of the background optical conductivities along the a-axis and the c-axis of $\kappa$-(BETS)$_2$FeBr$_4$ were obtained, which are presented in Figures 4.5(a) and 4.6(a) respectively. The various modes used to describe the background and phonons are demonstrated in Appendix B. The temperature dependence of the two strong phonon modes near 1277 cm$^{-1}$ and 1343 cm$^{-1}$ in the optical conductivity spectra of the a-axis and the c-axis respectively of $\kappa$-(BETS)$_2$FeBr$_4$ were further studied. Figures 4.7 and 4.8 show the temperature dependence of the fitting parameters for these two modes. It can be seen that these modes show strong asymmetry indicating coupling to the electronic background. Modes exhibiting a similar temperature dependence were observed in $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ near 1220 cm$^{-1}$ and 1330 cm$^{-1}$. [14] The other experimental phonon mode parameters can be found in Appendix C. One can see that most parameters appear to be affected near 60K.

Figures 4.5(a) and 4.6(a) show respectively the a-axis and c-axis Drude contribution (red curves) superimposed on the optical conductivity background with phonon features removed as determined from the oscillator fitting procedure. Along the a-axis as the temperature is lowered from 300K towards the maximum in the resistivity at 60K, the dc-conductivity (value of $\sigma_1$ at $\omega=0$) decreases. In this regime the scattering rate is very large. As the temperature is lowered further below 60K, the Drude absorption narrows considerably consistent with metallic behaviour. Note that along the a-axis the temperature variation of the background conductivity can not be explained entirely by the Drude contribution. Figures 4.5(b) and
4.6(b) show respectively the a-axis and c-axis the remaining contribution to the background conductivity after subtraction of the Drude component. Note that for the a-axis while at room temperature there remains a broad incoherent band, that as the temperature is lowered there is a redistribution of some of the spectral weight into a peak at lower frequencies. The position of this excitation shifts to lower frequency as the temperature decreases. Although it was not discussed, a similar feature is observed at 40K in the optical conductivity of the structurally isomorphic compound \( \kappa-(\text{BEDT-TTF})_2\text{Cu(NCS)}_2 \). [14] This behaviour is similar to that of the \((\text{TMTSF})_2\text{X}\) family of linear-chain organic conductors (\(\text{X} = \text{PF}_6, \text{AsF}_6\) or \(\text{ClO}_4\)) with the exception that in the \((\text{TMTSF})_2\text{X}\) materials the Drude component has very little spectral weight, and is very narrow, at all temperatures exhibiting essentially no overlap with the finite energy excitation. [15]

This similarity in the background conductivities of the two families of compounds is somewhat surprising. In the quasi one-dimensional \((\text{TMTSF})_2\text{X}\) materials the finite frequency peak was attributed to absorption above the Mott gap in a one-D Luttinger liquid. The zero frequency mode is assumed to exhibit Fermi Liquid behaviour and correspond to an energy scale below the 1D-2D crossover where hopping between chains is relevant.

Thus while the greater oscillator strength of the Drude component in the 2-D materials \(\kappa-(\text{BETS})_2\text{FeBr}_4\) and \(\kappa-(\text{BEDT-TTF})_2\text{Cu(NCS)}_2\) is consistent with this interpretation one would not expect to observe the finite frequency excitation. These combined works thus illustrate that there is still much to be learned concerning the optical properties of organic superconductors. Figure 4.6(a) and (b) show that the situation is somewhat different along the c-axis. The Drude peak is not as broad at high temperatures as it is along the a-axis, and upon its subtraction one observes an essentially temperature independent background conductivity.
Chapter 4. Experimental Data Analysis and Results

(a) a-axis

Optical Conductivity [1/(Ohm \* cm)]

Frequency [1/cm]

T — I — T — I — T — I — T — I

295K

150K

60K

45K

35K

25K

4K
Figure 4.5: Background optical conductivities along the a-axis. (a): The spectra in black color are background spectra with phonon modes removed; the spectra in red show the Drude contribution. (b): The background spectra with both Drude and phonon modes removed.
Chapter 4. Experimental Data Analysis and Results

(a) c-axis

Optical Conductivity [1/(Ohm*cm)]

Frequency [1/cm]

Temperature:
- 295K
- 150K
- 60K
- 45K
- 35K
- 25K
- 4K
Figure 4.6: Background optical conductivities along the c-axis. (a): The spectra in black color are background spectra with phonon modes removed; the spectra in red show the Drude contribution. (b): The background spectra with both Drude and phonon modes removed.
Chapter 4. Experimental Data Analysis and Results

(a) Phonon 1

Asym

Strength

ScatterRate[1/cm]

Wn[1/cm]

Temperature [K]
Figure 4.7: Temperature evolution of some phonon parameters along the a-axis of the sample. (a): Phonon 1 near 1277 cm$^{-1}$. (b): Phonon 2 near 1343 cm$^{-1}$. 
Chapter 4. Experimental Data Analysis and Results

(a) Phonon 1

- Asym
- Strength
- ScatterRate[1/cm]
- Wn[1/cm]

Temperature [K]

Values range from 0 to 300 Kelvin.
Figure 4.8: Temperature evolution of some phonon parameters along the c-axis of the sample. (a): Phonon 1 near 1277 cm\(^{-1}\). (b): Phonon 2 near 1343 cm\(^{-1}\).
4.3 Resistivity of $\kappa$-(BETS)$_2$FeBr$_4$

Based on the fitting parameters for the Drude mode, one can calculate the conductivity of a sample via equation (4.1):

$$\sigma = \frac{\omega_{PD}^2}{60\Omega \times \tau}, \tag{4.1}$$

where $\omega_{PD}$ is the plasma frequency of the Drude mode, and $\tau$ is the scattering rate both measured in cm$^{-1}$ and $\sigma$ is given in $\Omega^{-1}$cm$^{-1}$.

The resistivity is then calculated according to:

$$\rho = \frac{1}{\sigma}. \tag{4.2}$$

Therefore, using equations (4.1) and (4.2), the resistivities along the a-axis and the c-axis of $\kappa$-(BETS)$_2$FeBr$_4$ have been calculated at each temperature, and the results are presented in Figure 4.9. Note that the temperature variation is very similar to that of Figure 1.5.
Figure 4.9: Resistivities of $\kappa$-(BETS)$_2$FeBr$_4$ derived from Drude-model fitting to the optical conductivity.
Chapter 5

Conclusions

This thesis reports for the first time the optical functions of \( \kappa \)-\((\text{BETS})_2\text{FeBr}_4 \) in the infrared. The work has demonstrated that the optical properties of \( \kappa \)-\((\text{BETS})_2\text{FeBr}_4 \) have some similar features to those of both the 2-D organic superconductor \( \kappa \)-\((\text{BEDT-TTF})_2\text{Cu(}\text{NCS})_2 \) and the quasi 1-D \((\text{TMTSF})_2\text{X} \) materials, which may be important for understanding the optical properties of organic superconductors.

From Figure 4.5(b), one can see that the background optical conductivity spectrum of the a-axis of the sample gradually forms a peak at low frequency as temperature decreases from 295K to 4K. At higher temperatures the feature is relatively flat, but gradually becomes sharper and shifts to lower frequency with decreasing temperature. This pile up of the optical conductivity at low frequency and temperature might imply the presence of a gap in the electronic continuum. In contrast, from Figure 4.6(b), along the c-axis the background optical conductivity is essentially temperature independent, and thus along this axis the temperature dependence comes entirely from the Drude contribution.

The two most prominent phonon modes also show strong temperature dependence, with many parameters upon decreasing temperature showing abrupt changes with the onset of coherence at 60K. Their Fano shape indicates that they couple to the electronic background.

From the investigations of the resistivities along the a-axis and the c-axis shown in Figure 4.9, it can be concluded that these results agree with the general trend of the temperature dependence found in the relative ac-plane resistivity measurements from transport shown in Figure 1.5. That is, there is a maximum in the resistivity occurring around a temperature
of 60K, below which it begins to fall rapidly. Note that while the derived resistivity results of this work have poor temperature resolution they are to our knowledge the first reports of the absolute value of the resistivity along the a and c axes.

In future work, it would be very useful to repeat these experiments on much larger samples. In doing so, the optical conductivity of \( \kappa-(\text{BETS})_2\text{FeBr}_4 \) could be investigated at higher frequencies (higher than 2500 cm\(^{-1}\)). In addition, it would probably increase the accuracy of the results since there will be more signal in regions where the power spectrum is low if one were able to conduct each experiment on a new crystal whose surface has not been damaged by the gold evaporation process.
Appendix A

Resistivity Parameters for Hagen-Rubens Extrapolation

<table>
<thead>
<tr>
<th>$\rho$ ((\mu\text{Ohm} \cdot \text{cm}))</th>
<th>T(K)</th>
<th>4</th>
<th>25</th>
<th>35</th>
<th>45</th>
<th>60</th>
<th>150</th>
<th>295</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-axis</td>
<td></td>
<td>100</td>
<td>1000</td>
<td>3500</td>
<td>5000</td>
<td>9000</td>
<td>6000</td>
<td>5000</td>
</tr>
<tr>
<td>c-axis</td>
<td></td>
<td>200</td>
<td>250</td>
<td>1100</td>
<td>3500</td>
<td>7000</td>
<td>4200</td>
<td>3300</td>
</tr>
</tbody>
</table>

Table A.1: Resistivity.
Appendix B

Demonstration of Background Oscillator and Phonon Mode Fitting

As introduced in Chapter 4, several background oscillators and phonon modes were fitted to the experimental optical conductivity spectra such that the evolution of both the electronic background and the phonon modes with temperature could be studied. The following Figures B.1 and B.2 demonstrate the positions of these background oscillators and phonon modes and their experimental optical conductivity spectra. The fitted optical conductivity spectra of the a-axis and the c-axis at 35k were used to illustrate these modes for each axis respectively. The denotations used in these two Figures are also identical to those in the fitting parameter tables in Appendix C. Note that for the c-axis, the phonon 7 drawn as a dotted line appears only in the spectra at 4K and 25K.
Appendix B. Demonstration of Background Oscillator and Phonon Mode Fitting

Figure B.1: Fitting background oscillators and phonons of a-axis.

Figure B.2: Fitting background oscillators and phonons of c-axis.
Appendix C

Background Oscillator and Phonon Parameters

The following tables enumerate the parameters used to fit the experimental optical conductivities along the a-axis and c-axis respectively.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Drude</th>
<th>OSC1</th>
<th>OSC2</th>
<th>OSC3</th>
<th>OSC4</th>
<th>OSC5</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0</td>
<td>81.89</td>
<td>1581</td>
<td>12430</td>
<td>1800</td>
<td>2116</td>
</tr>
<tr>
<td></td>
<td>ω_n (cm^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>τ (cm^{-1})</td>
<td>39.5</td>
<td>16.63</td>
<td>7149</td>
<td>23300</td>
<td>337</td>
</tr>
<tr>
<td></td>
<td>ω_p</td>
<td>2592</td>
<td>1228</td>
<td>7666</td>
<td>14250</td>
<td>910.5</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>98.19</td>
<td>2141</td>
<td>12430</td>
<td>1800</td>
<td>2116</td>
</tr>
<tr>
<td></td>
<td>ω_n (cm^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>τ (cm^{-1})</td>
<td>557.3</td>
<td>59.2</td>
<td>3274</td>
<td>23300</td>
<td>337</td>
</tr>
<tr>
<td></td>
<td>ω_p</td>
<td>3469</td>
<td>966.8</td>
<td>5104</td>
<td>14250</td>
<td>723.8</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>35</td>
<td>0</td>
<td>147.6</td>
<td>2293</td>
<td>12430</td>
<td>1800</td>
<td>2116</td>
</tr>
<tr>
<td></td>
<td>ω_n (cm^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>τ (cm^{-1})</td>
<td>1118</td>
<td>145.2</td>
<td>3047</td>
<td>23300</td>
<td>337</td>
</tr>
<tr>
<td></td>
<td>ω_p</td>
<td>4062</td>
<td>1077</td>
<td>4402</td>
<td>14250</td>
<td>723.8</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table C.2: Continued Drude and Oscillator Parameters for a-axis.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>( \omega_n (cm^{-1}) )</th>
<th>( \tau (cm^{-1}) )</th>
<th>( \omega_p )</th>
<th>Asym</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>0</td>
<td>2155</td>
<td>4715</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>200.1</td>
<td>270.8</td>
<td>1320</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2233</td>
<td>2623</td>
<td>2982</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>12300</td>
<td>21060</td>
<td>13150</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1803</td>
<td>225.4</td>
<td>493</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2105</td>
<td>117.1</td>
<td>252.4</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>3058</td>
<td>3967</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>513.6</td>
<td>1789</td>
<td>3429</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2570</td>
<td>2152</td>
<td>2490</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>12080</td>
<td>20860</td>
<td>12980</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1786</td>
<td>462</td>
<td>975.2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2111</td>
<td>131.4</td>
<td>312</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>0</td>
<td>2566</td>
<td>4348</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>944.3</td>
<td>2000</td>
<td>2349</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2623</td>
<td>2112</td>
<td>2267</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>11860</td>
<td>19160</td>
<td>12070</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1789</td>
<td>423.8</td>
<td>896.7</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2140</td>
<td>244.8</td>
<td>419.9</td>
<td>0</td>
</tr>
<tr>
<td>295</td>
<td>0</td>
<td>2644</td>
<td>4946</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>885.1</td>
<td>1130</td>
<td>1531</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3564</td>
<td>3555</td>
<td>2673</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>12570</td>
<td>20270</td>
<td>11000</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1785</td>
<td>427.2</td>
<td>934.2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2124</td>
<td>278.1</td>
<td>526.9</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2644</td>
<td>1130</td>
<td>3555</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>20270</td>
<td>427.2</td>
<td>278.1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>11000</td>
<td>934.2</td>
<td>526.9</td>
<td>0</td>
</tr>
</tbody>
</table>
Table C.3: Phonon parameters for a-axis.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>( \omega_n (cm^{-1}) )</th>
<th>PH1</th>
<th>PH2</th>
<th>PH3</th>
<th>PH4</th>
<th>PH5</th>
<th>PH6</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td></td>
<td>1277</td>
<td>1353</td>
<td>1430</td>
<td>2384</td>
<td>285</td>
<td>252</td>
</tr>
<tr>
<td></td>
<td>( \tau (cm^{-1}) )</td>
<td>16.29</td>
<td>19.46</td>
<td>134.2</td>
<td>40</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>( \omega_p )</td>
<td>373.3</td>
<td>616</td>
<td>475.3</td>
<td>160</td>
<td>350</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0.2118</td>
<td>0.1934</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>( \omega_n (cm^{-1}) )</td>
<td>1278</td>
<td>1351</td>
<td>1430</td>
<td>2384</td>
<td>290</td>
<td>252</td>
</tr>
<tr>
<td></td>
<td>( \tau (cm^{-1}) )</td>
<td>20.23</td>
<td>26.92</td>
<td>134.2</td>
<td>40</td>
<td>22.57</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>( \omega_p )</td>
<td>429.7</td>
<td>678.7</td>
<td>475.3</td>
<td>160</td>
<td>440.5</td>
<td>176.9</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0.3153</td>
<td>0.2259</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>35</td>
<td>( \omega_n (cm^{-1}) )</td>
<td>1277</td>
<td>1347</td>
<td>1460</td>
<td>2384</td>
<td>290</td>
<td>252</td>
</tr>
<tr>
<td></td>
<td>( \tau (cm^{-1}) )</td>
<td>21.46</td>
<td>28.48</td>
<td>18.18</td>
<td>44.64</td>
<td>22.57</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>( \omega_p )</td>
<td>429.7</td>
<td>650</td>
<td>152.7</td>
<td>140</td>
<td>247</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0.3164</td>
<td>0.1825</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
### Appendix C. Background Oscillator and Phonon Parameters

<table>
<thead>
<tr>
<th>T(K)</th>
<th>( \omega_n , (cm^{-1}) )</th>
<th>( \tau , (cm^{-1}) )</th>
<th>( \omega_p )</th>
<th>Asym</th>
<th>( \omega_n , (cm^{-1}) )</th>
<th>( \tau , (cm^{-1}) )</th>
<th>( \omega_p )</th>
<th>Asym</th>
<th>( \omega_n , (cm^{-1}) )</th>
<th>( \tau , (cm^{-1}) )</th>
<th>( \omega_p )</th>
<th>Asym</th>
<th>( \omega_n , (cm^{-1}) )</th>
<th>( \tau , (cm^{-1}) )</th>
<th>( \omega_p )</th>
<th>Asym</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>1277</td>
<td>1346</td>
<td>1470</td>
<td>2399</td>
<td>286.5</td>
<td>252</td>
<td></td>
<td></td>
<td>1277</td>
<td>1343</td>
<td>1460</td>
<td>2377</td>
<td>285.4</td>
<td>242.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>21.49</td>
<td>30.93</td>
<td>18</td>
<td>30</td>
<td>10.19</td>
<td>10</td>
<td></td>
<td></td>
<td>25.93</td>
<td>38.23</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>388</td>
<td>588</td>
<td>135</td>
<td>120</td>
<td>137.9</td>
<td>94</td>
<td></td>
<td></td>
<td>453.2</td>
<td>667.1</td>
<td>238</td>
<td>150</td>
<td>150</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3986</td>
<td>0.2444</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>0.4006</td>
<td>0.2101</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1276</td>
<td>1343</td>
<td>1460</td>
<td>2377</td>
<td>285.4</td>
<td>242.2</td>
<td></td>
<td></td>
<td>1278</td>
<td>1341</td>
<td>1460</td>
<td>2394</td>
<td>289.7</td>
<td>247.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.93</td>
<td>38.23</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>15</td>
<td></td>
<td></td>
<td>31.74</td>
<td>54.11</td>
<td>40</td>
<td>40</td>
<td>22.23</td>
<td>19.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>453.2</td>
<td>667.1</td>
<td>238</td>
<td>150</td>
<td>150</td>
<td>200</td>
<td></td>
<td></td>
<td>433.2</td>
<td>661.6</td>
<td>200</td>
<td>155</td>
<td>160</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4006</td>
<td>0.2101</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>0.4892</td>
<td>0.187</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>1278</td>
<td>1342</td>
<td>1460</td>
<td>2394</td>
<td>285.4</td>
<td>254.3</td>
<td></td>
<td></td>
<td>1278</td>
<td>1342</td>
<td>1460</td>
<td>2394</td>
<td>285.4</td>
<td>254.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.74</td>
<td>54.11</td>
<td>40</td>
<td>40</td>
<td>22.23</td>
<td>19.54</td>
<td></td>
<td></td>
<td>35.39</td>
<td>74.1</td>
<td>40</td>
<td>10.68</td>
<td>7.81</td>
<td>13.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>433.2</td>
<td>661.6</td>
<td>200</td>
<td>155</td>
<td>160</td>
<td></td>
<td></td>
<td></td>
<td>360.9</td>
<td>631</td>
<td>130</td>
<td>103.9</td>
<td>87.55</td>
<td>130.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4892</td>
<td>0.187</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>0.5385</td>
<td>0.2178</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table C.4: Continued Phonon Parameters for a-axis.
<table>
<thead>
<tr>
<th>T(K)</th>
<th>Drude</th>
<th>OSC1</th>
<th>OSC2</th>
<th>OSC3</th>
<th>OSC4</th>
<th>OSC5</th>
<th>OSC6</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>(\omega_n (cm^{-1}))</td>
<td>0</td>
<td>1072</td>
<td>2812</td>
<td>19310</td>
<td>1792</td>
<td>2126</td>
</tr>
<tr>
<td></td>
<td>(\tau (cm^{-1}))</td>
<td>107.8</td>
<td>2041</td>
<td>1269</td>
<td>14980</td>
<td>1113</td>
<td>97.76</td>
</tr>
<tr>
<td></td>
<td>(\omega_p)</td>
<td>3622</td>
<td>4231</td>
<td>2649</td>
<td>13600</td>
<td>3192</td>
<td>320.6</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>(\omega_n (cm^{-1}))</td>
<td>0</td>
<td>861.4</td>
<td>2793</td>
<td>19310</td>
<td>1802</td>
<td>2126</td>
</tr>
<tr>
<td></td>
<td>(\tau (cm^{-1}))</td>
<td>84.25</td>
<td>2400</td>
<td>1113</td>
<td>14980</td>
<td>925</td>
<td>97.76</td>
</tr>
<tr>
<td></td>
<td>(\omega_p)</td>
<td>3052</td>
<td>4836</td>
<td>2546</td>
<td>13600</td>
<td>2618</td>
<td>372.7</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>35</td>
<td>(\omega_n (cm^{-1}))</td>
<td>0</td>
<td>625.3</td>
<td>2741</td>
<td>19310</td>
<td>1757</td>
<td>2160</td>
</tr>
<tr>
<td></td>
<td>(\tau (cm^{-1}))</td>
<td>345.1</td>
<td>2590</td>
<td>948.2</td>
<td>14980</td>
<td>644.8</td>
<td>409.3</td>
</tr>
<tr>
<td></td>
<td>(\omega_p)</td>
<td>3095</td>
<td>5857</td>
<td>2406</td>
<td>13600</td>
<td>2008</td>
<td>1013</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table C.6: Continued Drude and Oscillator Parameters for c-axis.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Drude</th>
<th>OSC1</th>
<th>OSC2</th>
<th>OSC3</th>
<th>OSC4</th>
<th>OSC5</th>
<th>OSC6</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>( \omega_n (cm^{-1}) )</td>
<td>0</td>
<td>675.3</td>
<td>2766</td>
<td>19310</td>
<td>1857</td>
<td>2260</td>
</tr>
<tr>
<td></td>
<td>( \tau (cm^{-1}) )</td>
<td>508.8</td>
<td>2265</td>
<td>1305</td>
<td>14980</td>
<td>972.3</td>
<td>685.3</td>
</tr>
<tr>
<td></td>
<td>( \omega_p )</td>
<td>2641</td>
<td>4769</td>
<td>2686</td>
<td>13600</td>
<td>2282</td>
<td>1249</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>( \omega_n (cm^{-1}) )</td>
<td>0</td>
<td>692.8</td>
<td>2796</td>
<td>19310</td>
<td>1857</td>
<td>2239</td>
</tr>
<tr>
<td></td>
<td>( \tau (cm^{-1}) )</td>
<td>526.3</td>
<td>2236</td>
<td>1252</td>
<td>14980</td>
<td>947.6</td>
<td>560.6</td>
</tr>
<tr>
<td></td>
<td>( \omega_p )</td>
<td>1876</td>
<td>4979</td>
<td>2803</td>
<td>13600</td>
<td>2159</td>
<td>1013</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>( \omega_n (cm^{-1}) )</td>
<td>0</td>
<td>741.4</td>
<td>2846</td>
<td>19310</td>
<td>1863</td>
<td>2251</td>
</tr>
<tr>
<td></td>
<td>( \tau (cm^{-1}) )</td>
<td>271.7</td>
<td>2126</td>
<td>1270</td>
<td>14980</td>
<td>921.2</td>
<td>564.7</td>
</tr>
<tr>
<td></td>
<td>( \omega_p )</td>
<td>1770</td>
<td>5013</td>
<td>2913</td>
<td>13600</td>
<td>2149</td>
<td>1049</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>295</td>
<td>( \omega_n (cm^{-1}) )</td>
<td>0</td>
<td>858.9</td>
<td>2874</td>
<td>19310</td>
<td>1797</td>
<td>2358</td>
</tr>
<tr>
<td></td>
<td>( \tau (cm^{-1}) )</td>
<td>249.8</td>
<td>1317</td>
<td>1388</td>
<td>14980</td>
<td>817.4</td>
<td>622.3</td>
</tr>
<tr>
<td></td>
<td>( \omega_p )</td>
<td>2109</td>
<td>5141</td>
<td>2811</td>
<td>13600</td>
<td>2946</td>
<td>1560</td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
### Table C.7: Phonon parameters for c-axis.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>PH1</th>
<th>PH2</th>
<th>PH3</th>
<th>PH4</th>
<th>PH5</th>
<th>PH6</th>
<th>PH7</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1280</td>
<td>1306</td>
<td>801.1</td>
<td>1160</td>
<td>278</td>
<td>176</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>(\omega_n (cm^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28.47</td>
<td>30.72</td>
<td>24.95</td>
<td>10.74</td>
<td>45.28</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>(\tau (cm^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>866.9</td>
<td>1008</td>
<td>433.3</td>
<td>170.9</td>
<td>1535</td>
<td>335.8</td>
<td>458.7</td>
</tr>
<tr>
<td></td>
<td>(\omega_p)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0.5435</td>
<td>0.1018</td>
<td>0.6869</td>
<td>0</td>
<td>0.0493</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>1280</td>
<td>1302</td>
<td>798.2</td>
<td>1160</td>
<td>230.3</td>
<td>168</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>(\omega_n (cm^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28.84</td>
<td>29.9</td>
<td>22.97</td>
<td>10.74</td>
<td>63.72</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>(\tau (cm^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>896.8</td>
<td>982.9</td>
<td>438</td>
<td>141.4</td>
<td>1464</td>
<td>233.9</td>
<td>323.1</td>
</tr>
<tr>
<td></td>
<td>(\omega_p)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0.5959</td>
<td>0.08881</td>
<td>0.5117</td>
<td>0</td>
<td>-0.2367</td>
<td>0</td>
</tr>
<tr>
<td>35</td>
<td>1277</td>
<td>1302</td>
<td>796.9</td>
<td>1164</td>
<td>242.7</td>
<td>168</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>(\omega_n (cm^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.69</td>
<td>28.58</td>
<td>20.96</td>
<td>10</td>
<td>51.8</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>(\tau (cm^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>971.6</td>
<td>889.7</td>
<td>461.6</td>
<td>141.1</td>
<td>518.8</td>
<td>378.8</td>
<td>1.729</td>
</tr>
<tr>
<td></td>
<td>(\omega_p)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Asym</td>
<td>0.5467</td>
<td>0.1043</td>
<td>0.3994</td>
<td>0</td>
<td>-0.02608</td>
<td>0</td>
</tr>
</tbody>
</table>
## Appendix C. Background Oscillator and Phonon Parameters

### Table C.8: Continued Phonon Parameters for c-axis.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>PH1</th>
<th>PH2</th>
<th>PH3</th>
<th>PH4</th>
<th>PH5</th>
<th>PH6</th>
<th>PH7</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>1274</td>
<td>1297</td>
<td>805.4</td>
<td>1159</td>
<td>231.7</td>
<td>173.3</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>48.37</td>
<td>34.02</td>
<td>47.94</td>
<td>10.74</td>
<td>44.98</td>
<td>31.01</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>886.9</td>
<td>667.5</td>
<td>403.2</td>
<td>148.7</td>
<td>456.4</td>
<td>272.1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.6373</td>
<td>0.05716</td>
<td>-0.0707</td>
<td>0</td>
<td>-0.2818</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>1275</td>
<td>1296</td>
<td>797.7</td>
<td>1156</td>
<td>228.9</td>
<td>177.2</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>39.91</td>
<td>31.54</td>
<td>59.46</td>
<td>10.74</td>
<td>39.21</td>
<td>29.95</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>834.7</td>
<td>677.5</td>
<td>381.2</td>
<td>159.8</td>
<td>331</td>
<td>181.3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.6138</td>
<td>0.04944</td>
<td>-0.2868</td>
<td>0</td>
<td>-0.4716</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>1274</td>
<td>1296</td>
<td>799.4</td>
<td>1159</td>
<td>238.4</td>
<td>169.7</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>38.26</td>
<td>28.69</td>
<td>48.15</td>
<td>10.74</td>
<td>30.44</td>
<td>51.9</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>837.5</td>
<td>659.5</td>
<td>347</td>
<td>147.8</td>
<td>376.8</td>
<td>298.5</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.5949</td>
<td>0.03659</td>
<td>-0.2064</td>
<td>0</td>
<td>-0.3671</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>295</td>
<td>1260</td>
<td>1307</td>
<td>795.5</td>
<td>1159</td>
<td>226.6</td>
<td>176.4</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>38.04</td>
<td>58.4</td>
<td>25.05</td>
<td>10</td>
<td>93.92</td>
<td>75.5</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>848.3</td>
<td>888.4</td>
<td>580.5</td>
<td>161.6</td>
<td>834.9</td>
<td>709.5</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.4943</td>
<td>0.2398</td>
<td>0.1782</td>
<td>0</td>
<td>-0.3844</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Bibliography


