INFRARED OPTICAL PROPERTIES OF THE ORGANIC SUPERCONDUCTOR \((BEDT-TTF)_2[Cu(NCS)_2]\) AND THE SEARCH FOR THE SUPERCONDUCTING GAP

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

Doctor of Philosophy

in

THE FACULTY OF GRADUATE STUDIES

DEPARTMENT OF PHYSICS

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

November 1990

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Abstract

The optical properties of the 10.4 K organic superconductor, \( \kappa-(BEDT-TTF)_2[CU-(NCS)_2] \), are the subject of this thesis. This organic superconductor is a crystalline solid consisting of planes of \( BEDT-TTF \) molecules separated by planes of \( Cu(NCS)_2 \) anions. The arrangement of molecules results in electrical two-dimensionality, with high conductivity within the planes of \( BEDT-TTF \) molecules and poor conductivity in the perpendicular direction. Until the recent discovery of an organic superconductor with \( T_c = 11.5 \) K, the 10.4 K transition of \( (BEDT-TTF)_2[Cu(NCS)_2] \) was the highest in the class of organic metals.

Optical properties of superconductors have played an important role in analysis of their unusual properties. Using single crystals of \( (BEDT-TTF)_2[CU(NCS)_2] \) and light polarized within the highly conducting plane, I have measured both specular reflectivity and bolometric absorption over a wide region of the infrared spectrum. The reflectivity measurements cover most of the far and mid-infrared for both protonated and deuterated compounds, with sample temperatures between 300 K and 6.5 K. The resulting spectra show contributions from electronic interband transitions, intraband transitions, and molecular phonon vibrations.

A search for the superconducting energy gap was undertaken using the bolometric technique to measure the sample absorption at far-infrared energies. These measurements were performed at temperatures below \( T_c \) and cover the part of the spectrum where condensation of electrons into superconducting Cooper pairs should be directly observable optically. On other materials, measurements in this part of the spectrum have directly revealed the binding energy for the superconducting electron pairs, and
have been instrumental in showing that details of the electron–phonon interactions are very important in superconducting systems. In the spectra which we have measured, any effect of the superconducting transition is overwhelmed by other contributions to the absorption in the far–infrared energy region.
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Acknowledgements

I would like to thank Dr. J. E. Eldridge for his many useful suggestions and his encouragement throughout the course of my studies. The same goes for my lovely, talented, and most patient wife, Nikki, who also played a vital role in providing timely suggestions and in proof-reading this thesis.

The work of Chris Homes, whose work as a graduate student in this laboratory has closely paralleled mine, also played an important role in the work presented here. One of Chris’s abilities (of which there are many) for which I am particularly grateful is his expertise as a computer hack, which led to his writing the program for the phase-phonon model calculations.

The expertise of the technical support staff in the Physics department and on campus here at U.B.C. is also appreciated. In particular, I would like to thank Jack Bosma in the student machine shop, all the technicians in both the main departmental machine shop and in the electronics shop, and the computer support staff. I would also like to thank the secretaries who have always made sure that I registered for courses and paid my fees.

During this research I have been supported by the University of British Columbia and the Province of British Columbia. This work was also supported by Grant No. A5653 from the Natural Sciences and Engineering Research Council of Canada.
Chapter 1

Introduction

Discoveries of several new superconducting materials have made the last few years very exciting for many solid state physicists. Heavy fermion, organic, and high-$T_c$ ceramic materials all display superconductivity and raise the possibility of novel mechanisms for superconductivity. In all three cases, there are measurements pointing to the inadequacy of the ordinary BCS phonon-coupling picture. The unique characteristics of these new superconductors have stimulated development of new theories for possible superconducting mechanisms and extraordinary claims for the possibilities of superconductivity at high temperatures.

1.1 Organic Conductors and Superconductors

1.1.1 History

One of the first serious proposals for an organic substance with metallic properties which might exhibit high temperature superconductivity was put forward by W. A. Little in 1964[1]. His idea was to make a material with linear conducting chains surrounded by easily polarizable organic side groups. The analysis was analogous to that of the conventional BCS theory except that the attractive force would be mediated by electrical polarization rather than by phonons. Conduction electrons moving along the chains would induce an electric polarization resulting in a net attractive force for other nearby electrons. The speculation was that because the mechanism involves movement of light
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electrons rather than heavy atoms, the excitation might be effective on a higher energy scale than the BCS phonon mechanism. Claims were made that such a system might remain in a superconducting state at temperatures as high as 2000 K.

Little's concept was received with great interest and stimulated a lot of research on organic crystals with low dimensionality. Some fairly good conductors were developed using either linear chain polymers such as \((CN)\_x\) or by stacking molecules such as \(TTF\) and \(TCNQ\) in charge transfer salt systems [2, 3]. Some of the common building blocks for organic conductors, all of which are similar to the \(TTF\) and \(TCNQ\) molecules, are shown in Figure 1.1. In the charge transfer salt systems, crystals are grown by combining these large, nearly flat molecules with other molecules with the opposite electron affinity to form an ionic solid. In many of the best conductors the large organic molecule becomes the cation and is combined with the anions in a ratio of 2:1. For example, in \((TMTSF)_2PF_6\) and \((BEDT-TTF)_2[Cu(NCS)_2]\) the unit cell contains one anion having a charge of \(-1\) and a pair of cations with an average charge of \(+\frac{1}{2}\) each. Figure 1.2 shows how the molecules are arranged in stacks in the \((TMTSF)_2PF_6\) compound. This type of linear chain structure is seen in many of the organic conductors and leads to highly anisotropic electronic properties. For \((TMTSF)_2PF_6\), the ratio of electrical conductivities along the three crystallographic axes is \(10^4:100:1\).[4]

An early organic conductor was made using stacked \(TTF\) and \(TCNQ\) molecules, with the resulting material having conductivity increasing with decreasing temperature to a maximum of \(10^4 (\Omega \text{cm})^{-1}\) before a semiconducting transition terminated the metallic behaviour[3]. It soon became clear that one-dimensional systems in general prefer to be in a semiconducting state at low temperature. In 1954, Peierls showed that for any purely one-dimensional system, it is energetically favourable for a gap to open in the band structure at the Fermi wavevector \(k_f\) as shown in Figure 1.3[8]. Physically, the material undergoes a distortion towards unequal electron spacing along the stack (see Figure 1.4)
Figure 1.1: Some of the molecules used in making organic conductors. **TTF** is short for tetrathiafulvalene where *tetrathia* refers to the four sulfur atoms replacing carbons in the fulvalene ring. **TMTSF** is a modification of the basic **TTF** molecule with selenium replacing the sulfurs and extra methyl groups on the ends. Thus the full name is tetramethyltetraselenafulvalene. **BEDT-TTF** is a further modification of the basic **TTF** molecule with extra ethylene groups joined to each end using two more sulfur atoms. These additions give **BEDT-TTF** the full chemical name, *bis*- (ethylenedithio) tetra-thiafulvalene[5].
Figure 1.2: Organic molecules such as those shown in Figure 1.1 can be stacked to form nearly one-dimensional conducting chains in a solid. (a) This side view of the (TMTSF)$_2$-PF$_6$ structure shows two stacks of the large, flat TMTSF molecules and the positions of the octahedral PF$_6^-$ anions. (b) View looking down the stack of TMTSF molecules[6, 7].
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Figure 1.3: For a one-dimensional material, the Peierls distortion leads to a gap in the energy bands at the Fermi level. With such a gap, the material is a semiconductor at low temperatures [9].

with a resulting change in the electrical properties from metallic to semiconducting. The property which makes the one-dimensional system unique is that the Fermi surface is a sheet and all electrons at $k_f$ enjoy the reduction in energy. If the system had higher dimensionality, the first order approximation of the Fermi surface would be either a cylinder (2D) or a sphere (3D) and a lattice distortion could not open a gap on the entire Fermi surface. For the one-dimensional system the Peierls state can take the form of a lattice distortion, a spin-density-wave (SDW) or a charge-density-wave (CDW). In all three cases the gap destroys the possibility of metallic behaviour.

The first organic conductors to overcome the tendency towards Peierls instability and
Figure 1.4: In real space, the Peierls transition is seen in a charge density wave with wavevector $k_f$ [6].

exhibit superconductivity were developed by Klaus Bechgaard in the late 1970's[6]. This class of materials, now known as the Bechgaard salts, is based on the TMTSF molecule shown in Figure 1.1. In these materials, chains of TMTSF molecules are arranged in sheets which are separated by planes containing anions as shown previously in Figure 1.2. A wide variety of anions can be substituted including octahedral molecules like $PF_6^-$ and $AsF_6^-$ or tetrahedral molecules like $ReO_4^-$ and $ClO_4^-$. Electrical conductivity in the sheets of TMTSF molecules is allowed through overlap of the selenium atom electron orbitals. There is also enough overlap between neighbouring stacks to give some two-dimensionality and reduce, but not eliminate, the tendency towards a Peierls transition.

At room temperature, most of the Bechgaard salts behave as metals with conductivity increasing as the temperature is lowered. However, the metallic properties disappear with the onset of either an anion-ordering transition or a spin-density-wave state, except for those samples made with the $ClO_4^-$ anion[7]. Measurements of dc resistance, shown in
Figure 1.5, demonstrate the onset of semiconducting behaviour for several of the Bechgaard salts. The anion ordering transition occurs in the materials containing anions with tetrahedral symmetry such as $BF_4^-$. The symmetry of these molecules allows them to assume two crystallographically distinct orientations in the lattice. At room temperature, thermal motion keeps the tetrahedral anions from being fixed in any particular orientation, but as the temperature is lowered, neighbours assume alternating orientations. This leads to a distortion of the lattice and a transition from metallic to semiconducting behaviour. The materials with octahedral anions undergo a spin–density–wave transition. This is a Peierls-type transition in which the spins of the conduction electrons become ordered antiferromagnetically with wavevector $2k_f$. The antiferromagnetic spin–density–wave, illustrated in Figure 1.6, is similar to the charge–density–wave in the effect it has in introducing a gap at the Fermi level, destroying the possibility of metallic behaviour. Application of pressure, usually between 5 kbar and 10 kbar, increases the two–dimensionality of these materials enough to suppress the semiconducting transitions.

The first organic superconductivity was observed in 1979 with the $(TMTSF)_2PF_6$ compound at a temperature of 0.9 K and under 8 kbar of pressure[10]. The phase diagram for $(TMTSF)_2PF_6$ in Figure 1.7 is typical of these materials. The only ambient–pressure superconductor in this class of organic conductors is obtained with $ClO_4^-$ as the anion which, when slowly cooled, demonstrates a superconducting transition at 1.4 K[11].

Recently, much higher superconducting temperatures have been achieved with the development of organic metals based on the $BEDT–TTF$ (or more commonly just ET) molecule which is shown in Figure 1.1[14, 15]. An ET molecule is very similar to the $TMTSF$ of the Bechgaard salts except that at each end there are extra sulfur atoms attaching to ethylene groups. As with the Bechgaard salts, ionic solids with metallic properties can be made using the ET molecule in combination with a variety of anions. The crystalline configurations of the ET materials are also similar to the Bechgaard
Figure 1.5: Most of the Bechgaard type organic conductors become semiconductors at low temperature. This figure shows the electrical resistance for several of the Bechgaard salts in the temperature range of the Peierls transition[12].
Figure 1.6: The spin-density-wave in TMTSF compounds is shown here in the lower curve while the accompanying charge-density-wave is shown above. Each of the circles represents the position of a TMTSF molecule and the arrow indicates the direction of the electron spin[7].

salts in that they contain highly conducting planes of the organic molecules separated by planes of anions. Many new phases are possible, however, because the ET molecules are not restricted to the simple linear stack formation. In many of the new phases, the electronic properties are nearly two-dimensional and the tendency towards a Peierls semiconducting transition is mostly eliminated.

One of the most important of the new ET phases is the $\kappa$ arrangement illustrated in Figure 1.8. Here the highly conducting plane contains pairs of molecules arranged with alternating orientation to fill the plane. This results in a crystal with almost perfectly isotropic two-dimensional electrical properties. The two highest temperature organic superconductors, $(BEDT-TTF)_2[Cu(NCS)_2]$ with $T_c=10.4$ K and $BEDT-TTF)_2Cu[\text{N(CN)}_2]Br$ with $T_c=11.5$ K are both $\kappa$ phase materials.
Figure 1.7: The phase diagram for $(\text{TMTSF})_2\text{PF}_6$ shows the spin–density–wave semiconducting region at low pressures and the onset of a superconducting region at a pressure of 8 kbar and 0.9 K[13].
Figure 1.8: In a $\kappa$ phase crystal, the highly conducting plane consists of pairs of $ET$ molecules with alternating orientation. Looking down on the $ET$ conducting plane as in this diagram, the long $ET$ axis is perpendicular to the page. The larger circles represent the sulfur atoms while the smaller ones represent carbons[16].
Table 1.1 shows the critical temperatures and pressures of many of the known organic superconducting materials. At present, there are more than 30 different organic superconductors[5]. The group of ET based materials contribute at least 17 of the superconductors with transition temperatures ranging from below 1 K up to the current record of 11.5 K[17]. Bechgaard salts contribute 7 more superconducting compounds, while several of the more esoteric variations of the basic charge transfer salts contribute a few other interesting materials.

1.1.2 General Properties of the \((BEDT-TTF)_{2}[Cu(NCS)_{2}]\) Organic Superconductor

Organic metals exhibit many interesting features in addition to low temperature superconductivity. This section presents an overview of measurements and calculations which have been performed for the \(T_{c}=10.4\) K ET salt \((BEDT-TTF)_{2}[Cu(NCS)_{2}]\). It includes the published calculated electronic band structure along with measurements of the crystal structure, electrical conductivity, thermopower, magneto-resistance, and magnetic properties.

Crystal Structure

The names BEDT – TTF and ET are abbreviations for the full chemical name of our building block molecule, \(bis\)-(ethylenedithio) tetrathiafulvalene. To explain how this name is derived, it is best to start at the end and work towards the beginning (while looking at the representation of the ET molecule in Figure 1.1). The word fulvalene is used by chemists to describe the central grouping of a double carbon bond joining two rings of carbon atoms. When four of the carbons in the rings are replaced with sulfurs, the prefix tetra-thia is added since thia or thio is used instead of the word sulfur in organic chemistry formulas. At this stage, we have tetra-thia-fulvalene or TTF for
Table 1.1: List of Organic Superconductors. Greek letters in front of the \textit{BEDT} – \textit{TTF} based formulas indicate specific structural phases[5, 7].

<table>
<thead>
<tr>
<th>Material</th>
<th>( P_c(\text{kbar}) )</th>
<th>( T_c(K) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((SN)_2)</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>((TMTSF)_2PF_6)</td>
<td>6.5</td>
<td>1.2</td>
</tr>
<tr>
<td>((TMTSF)_2AsF_6)</td>
<td>12</td>
<td>0.9</td>
</tr>
<tr>
<td>((TMTSF)_2SbF_6)</td>
<td>11</td>
<td>0.4</td>
</tr>
<tr>
<td>((TMTSF)_2TaF_6)</td>
<td>12</td>
<td>1.4</td>
</tr>
<tr>
<td>((TMTSF)_2ClO_4)</td>
<td>0</td>
<td>1.4</td>
</tr>
<tr>
<td>((TMTSF)_2ReO_4)</td>
<td>12</td>
<td>1.3</td>
</tr>
<tr>
<td>((TMTSF)_2FSO_3)</td>
<td>6</td>
<td>3.0</td>
</tr>
<tr>
<td>((BEDT - TTF)_4(ReO_4)_2)</td>
<td>4.5</td>
<td>2.0</td>
</tr>
<tr>
<td>(\beta - (BEDT - TTF)_3I_3)</td>
<td>0</td>
<td>1.4</td>
</tr>
<tr>
<td>(\beta^* - (BEDT - TTF)_2I_3)</td>
<td>0.5</td>
<td>7.6</td>
</tr>
<tr>
<td>(\gamma - (BEDT - TTF)<em>3I</em>{2.5})</td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>(\epsilon - (BEDT - TTF)_2I(I_8)_0.5)</td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>(\alpha - (BEDT - TTF)_2I_3 : I_2)-doped</td>
<td>0</td>
<td>3.3</td>
</tr>
<tr>
<td>(\alpha t - (BEDT - TTF)_2I_3)</td>
<td>0</td>
<td>8.0</td>
</tr>
<tr>
<td>(\theta - (BEDT - TTF)_2I_3)</td>
<td>0</td>
<td>3.6</td>
</tr>
<tr>
<td>(\kappa - (BEDT - TTF)_2I_3)</td>
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<td>3.6</td>
</tr>
<tr>
<td>(\beta - (BEDT - TTF)_2IBr_2)</td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>(\beta - (BEDT - TTF)_2AuI_2)</td>
<td>0</td>
<td>4.2</td>
</tr>
<tr>
<td>((BEDT - TTF)<em>4Hg</em>{2.88}Cl_8)</td>
<td>0</td>
<td>4.2</td>
</tr>
<tr>
<td>((BEDT - TTF)<em>4Hg</em>{2.88}Br_8)</td>
<td>12</td>
<td>1.8</td>
</tr>
<tr>
<td>((BEDT - TTF)_3Cl_2(H_2O)_2)</td>
<td>16</td>
<td>2.0</td>
</tr>
<tr>
<td>((BEDT - TTF)_2[\text{Cu(NCS)}_2])</td>
<td>0</td>
<td>10.4</td>
</tr>
<tr>
<td>((BEDT - TTF)_2Cu[\text{N(CN)}_2]Br)</td>
<td>0</td>
<td>11.5</td>
</tr>
<tr>
<td>((DMET)_2Au(CN)_2)</td>
<td>1.5</td>
<td>0.9</td>
</tr>
<tr>
<td>((DMET)_2AuI_2)</td>
<td>5</td>
<td>0.6</td>
</tr>
<tr>
<td>((DMET)_2AuBr_2)</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>((DMET)_2AuCl_2)</td>
<td>0</td>
<td>0.9</td>
</tr>
<tr>
<td>((DMET)_2I_3)</td>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td>((DMET)_2IBr_2)</td>
<td>0</td>
<td>0.7</td>
</tr>
<tr>
<td>(\text{TTF}[\text{Ni(dmit)}]_2)</td>
<td>7</td>
<td>1.6</td>
</tr>
<tr>
<td>((CH_3)_{4}\text{N}[\text{Ni(dmit)}]_2)</td>
<td>7</td>
<td>5.0</td>
</tr>
</tbody>
</table>
short. The next prefix is *bis-(ethylene-di-thio)* or *BEDT*. *Bis* means that everything in the brackets happens twice. *Ethylene-di-thio* describes an ethylene \((C_2H_6)\) molecule with two hydrogens replaced by sulfurs. Using the extra sulfur atom valence electrons, one of these *EDT* groups joins onto each end of the central *TTF* to give the outer rings, each with four carbons and two sulfurs. Bringing all this together gives the full name *bis-(ethylenedithio)* tetrathiafulvalene.

Molecular arrangements in the crystalline *ET* solids are partly determined by the size and shape of the basic *ET* molecule. The outer *BEDT* rings give *ET* molecules four extra sulfur atoms compared to *TMTSF*. This is important because it is mainly the sulfur electron orbitals which overlap with neighbouring molecules in the solid to allow electrical conduction and to determine the lattice spacing. For the *ET* based solids, these extra sulfurs contribute to electron orbital overlap not just vertically along a stack but also horizontally between adjacent molecules. This generally gives the *ET* based compounds more two-dimensionality and enables them to deviate from the strictly one-dimensional stacks common to the *TMTSF* materials.

By escaping the restriction of one-dimensional arrangements, the *ET* based materials show a wide diversity of crystal structures. An advantage of this is that it is relatively easy to obtain many different materials with new physical properties. A disadvantage is that each crystal which is grown has to be analysed to definitively characterize the structure. A brief review of the literature reveals *ET* based solids with \(\alpha, \beta, \delta, \epsilon, \gamma, \kappa, \eta, \) and \(\theta\) phases\[19, 20, 21, 22, 23, 24, 25\]. In most cases, the different phases indicate either a relative displacement of *ET* stacks or a difference in orientation for molecules from different stacks. For example, the structures for the \(\alpha, \beta\) and \(\theta\) phases are shown in Figure 1.9.

The \(\kappa\) phase is the one new arrangement where one-dimensional stacking is completely absent. Crystallographically, \(\kappa-(BEDT-TTF)_2[Cu(NCS)]_2\) is monoclinic with \(P2_1\)
Figure 1.9: Planes containing the ET molecules are shown here for the α, β, and θ phases. There are differences between the stack displacements and orientations of molecules in different stacks. [20, 25]
space group symmetry[18]. A monoclinic system is defined by having 90 degrees for two of the three angles between the unit cell axes. $P2_1$ symmetry means that there is one screw axis for which a 180 degree rotation followed by a translation along the axis brings all molecules and atoms back to crystallographically equivalent positions. The asymmetrical arrangement of $Cu(NCS)_2$ anions in this crystal removes an additional glide plane symmetry which gives many other $\kappa$ phase materials $P2_1/c$ space group symmetry.

Several diagrams of the $\kappa$ phase crystalline structure follow in the hope that including more than one view will help make the physical picture clearer. All the data used to create these diagrams was obtained using x-ray diffraction because the organic samples are always small and are not usually made in large enough quantities to allow neutron scattering studies. In Figure 1.8, the checkerboard arrangement of $ET$ molecules in the highly conducting plane is shown. From this perspective, the long axes of the $ET$ molecules are perpendicular to the plane of the paper. The planes of $Cu(NCS)_2$ anions sitting above and below the $ET$ structure are added in Figure 1.10. Each $Cu(NCS)_2$ unit has a “V” shape with $Cu$ at the vertex and almost linear $NCS$ arms. These units join together to make a continuous polymer chain along the $b$ axis[26]. The stacking fault shown in Figure 1.10 is only seen in this particular data and is not a commonly seen feature of the structure. In Figure 1.11, a similar view is illustrated including labels for distances between nearest neighbour sulfur atoms in the $ET$ plane[18]. As shown in Table 1.2, these distances are roughly the same in all directions, demonstrating the isotropic nature of the material. Figure 1.12 is a slightly more confusing picture since neither the molecular arrangement nor the plane-like features of the structure are easily visible. This diagram is included to show that it is the long $ET$ axis which bridges the gap between the anion planes.

One unique feature of the $\kappa$-(BEDT-TTF)$_2[Cu(NCS)_2]$ salt is the temperature
Figure 1.10: This diagram shows the \((BEDT-TTF)_2[Cu(NCS)_2]\) crystals structure from the same point of view as in Figure 1.8 This time, the linear chain structure of the \(Cu(NCS)_2\) anion plane lying above the ET plane is included[26].
Figure 1.11: This is a view of the $\kappa$ similar to those shown in Figures 1.8 and 1.10. Nearest neighbour distances are labelled and values of $t$, $u$, $v$ and $w$ are listed in Table 1.2.\[18\]
Figure 1.12: This diagram is included to show the way in which the long axis of the ET molecules spans the gap between planes of Cu(NCS)$_2$ anions in (BEDT-TTF)$_2$[Cu-(NCS)$_2$]. The angle, $\beta$, between the $a$ and $c$ axes is 110 degrees[18].
Table 1.2: Nearest neighbour distances for sulfur atoms in $\kappa-(BEDT-TTF)_2[Cu(NCS)_2]$. Figure 1.12 defines the labels S1 to S16 for the 16 different sulfur atoms within a unit cell[18].

<table>
<thead>
<tr>
<th></th>
<th>298K</th>
<th>104K</th>
</tr>
</thead>
<tbody>
<tr>
<td>t</td>
<td>S1-S13</td>
<td>3.659(5)</td>
</tr>
<tr>
<td>u</td>
<td>S3-S13</td>
<td>3.554(7)</td>
</tr>
<tr>
<td>v</td>
<td>S8-S16</td>
<td>3.553(8)</td>
</tr>
<tr>
<td></td>
<td>S6-S16</td>
<td>3.574(8)</td>
</tr>
<tr>
<td></td>
<td>S3-S9</td>
<td>3.508(8)</td>
</tr>
<tr>
<td></td>
<td>S3-S11</td>
<td>3.510(9)</td>
</tr>
<tr>
<td>w</td>
<td>S2-S16</td>
<td>3.671(7)</td>
</tr>
</tbody>
</table>

Table 1.3: Crystallographic parameters for $\kappa-(BEDT-TTF)_2[Cu(NCS)_2]$ at 298 K and 104 K[18].

<table>
<thead>
<tr>
<th></th>
<th>298 K</th>
<th>104 K</th>
<th>$(\Delta l/l) \times (1/\Delta T)(\times K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a/\AA$</td>
<td>16.248(5)</td>
<td>16.382(4)</td>
<td>$4.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>$b/\AA$</td>
<td>8.440(2)</td>
<td>8.402(2)</td>
<td>$-2.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>$c/\AA$</td>
<td>13.1224(5)</td>
<td>12.833(4)</td>
<td>$-11.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\beta/(\text{degrees})$</td>
<td>110.30(3)</td>
<td>111.33(2)</td>
<td>$4.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>$V/\AA^3$</td>
<td>1688.0(9)</td>
<td>1645.3(7)</td>
<td>$-13.0 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

dependence of the lattice spacing. Unit cell parameters have been measured at 298 K and 104 K and are illustrated in Table 1.3. Thermal contraction is very anisotropic with both of the highly conducting $b$ and $c$ axes contracting while the perpendicular $a$ axis expands slightly. Such anisotropic temperature dependence indicates that there is a slight change in the optimal crystalline configuration which is most likely due to the ET molecule ethylene end groups freezing in position at the lower temperature[18]. This temperature dependent lattice structure is probably important in explaining features of the dc-resistivity measurements which are shown in the next section.
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Electrical Conductivity

Measurements of dc-conductivity also illustrate the unusual behaviour of these organic metals. In addition to revealing the transition to the superconducting state, $R(T)$ has very unusual temperature dependence, unlike either ordinary metals or semiconductors.

There is good agreement among the many groups which have measured the dc-resistivity [16, 27, 28, 29, 30, 31, 32]. At room temperature, the conductivity in the highly conducting plane is relatively low, of the order of $20(\Omega\text{cm})^{-1}$. In the poorly conducting third direction, perpendicular to the planes, the conductivity is lower by a factor of approximately 600[30]. Within the high-conductivity plane, the resistivity decreases slightly between room temperature and 250 K at which point there is a gradual increase up to about double the room temperature resistance at 110 K. Further cooling once again establishes normal metallic properties below 90 K until the superconducting transition at 10.4 K. An example of a typical measurement is shown in Figure 1.13.

The origin of the resistance maximum near 100 K becomes clearer in measurements shown in Figure 1.14 which were performed with the sample subjected to external pressure. Under these conditions the resistivity peak changes drastically, becoming progressively sharper at pressures of 0.9 kbar and 2 kbar before abruptly disappearing in all measurements above 3 kbar. It is clear from the 2 kbar measurement that the sample is in a metallic state above 100 K and undergoes an abrupt phase transition to another lower conductivity metallic state at lower temperature. This metal–metal phase transition is probably connected to the unusual temperature dependence of the lattice structure. Because the electrical properties of organic conductors are very sensitive to subtle changes in electron orbital overlaps, it is most likely that the 100 K electronic transition will be associated with structural rearrangements at this temperature.

One group has presented an argument that the observed dc-resistivity curves might
Figure 1.13: \((\text{BEDT-TTF})_2[\text{Cu(NCS)}_2]\) dc-resistance as a function of temperature[32].
Figure 1.14: Resistance as a function of temperature for \((BEDT-TTF)_2[Cu(NCS)_2]\) under external pressure. The 2 kbar curve gives a clear indication of a metal-metal phase transition which disappears at higher pressures[31].
be explained by a model of an insulator–metal transition [33]. Simply stated, their explanation is that the thermal contraction of the lattice would gradually broaden the valence and conduction bands for a semiconducting material. Eventually, the bands would start to overlap and cause a change from semiconducting to metallic behaviour. Unfortunately, their argument is based on the pressure dependent measurements shown in Figure 1.15 which concentrate on higher pressures and miss the interesting and important features below 3 kbar [29].

Application of pressure also has a strong effect on $T_c$ for the $(BEDT–TTF)_2[Cu(NCS)_2]$ salt. The measured resistivity in Figure 1.15 shows the rapidly dropping transition temperature with applied pressure. Similar results are obtained using an rf impedance technique to determine $T_c$ with the results for various ET superconductors shown in Figure 1.16 [34]. It is suggested that the initial decrease of $dT_c/dP = -3 \, K/kbar$ is the largest recorded value for any superconductor.

Electronic Band Structure

Electronic properties of solids can only be fully explained in terms of the electronic band structure. The band structure consists of a representation of the allowed electron energy states in momentum (or $k$) space such as shown in Figure 1.3 for the simple one-dimensional solid. There is a direct relationship between the band structure and measured quantities such as electrical conductivity, the effective mass of charge carriers, thermoelectric power, optical conductivity and magneto-resistance. Thus, knowledge of the correct band structure is at the heart of explaining physical properties on a fundamental level.

The general procedure used to obtain reliable band structures is to perform the best possible calculation and then check for agreement with experimental results. The experiments which have been performed on organic conductors which relate most directly to
Figure 1.15: $T_c$ drops rapidly with application of pressure in $(BEDT-TTF)_2Cu(NCS)_2$ as is demonstrated in this plot of resistance versus temperature$^{[29]}$. 
Figure 1.16: The decrease in $T_c$ with applied pressure is more dramatic in the $Cu(NCS)_2$ compound than in other ET based superconductors[34].
the band structure are those based on the Shubnikov–de Haas technique. These mea-
surements reveal only details of the Fermi surface, not the entire band structure, because
they are only sensitive to the most energetic electrons at the top of the bands. However,
even these limited results are quite useful for confirmation of calculations because they
give such a direct picture of the allowed momentum states at the Fermi surface.

Much effort has gone into computer models and calculations for ET based organic
materials[35, 36, 37, 38]. The more reliable of these calculations are based on a tight
binding model [35, 36, 38]. The computer program starts by calculating bound electron
wavefunctions for isolated molecules and proceeds to calculate the intermolecular overlap
of the highest occupied molecular orbitals (HOMO), the transfer integrals for electrons
moving between molecules, and finally the band structure and Fermi surface using the
tight binding model[35]. This type of calculation requires a great deal of supercomputer
time, especially for a material such as \((BEDT−TTF)_2[Cu(NCS)_2]\) where there are over
100 atoms in a unit cell.

Results of band structure calculations for \((BEDT−TTF)_2[Cu(NCS)_2]\) are shown
in Figure 1.17. Metallic properties result from the half-filling of the upper band due
to the loss of \(\frac{1}{2}\) electron per ET molecule. A cross section of the Fermi surface in the
repeated zone scheme is shown in Figure 1.18(a). The surface is a slightly distorted
cylinder which bulges out over the Brillioun zone along the \(M−Z\) boundary. At the
intersections along the \(M−Z\) boundary the bands interact and split, effectively separating
a continuous one-dimensional piece and a small ellipse-like two-dimensional piece as
shown in Figure 1.18(b). The calculated area of the ellipse is 18% of the Brillouin zone.
It should be remembered that this is a cross sectional view so the one-dimensional part
is a really a sheet and the two-dimensional part is a cylinder.

Shubnikov–de Haas experiments, which provide the best supporting evidence for the
calculated band structure, are performed by measuring dc electrical conductivity in a
Figure 1.17: The calculated band structure of \((BEDT-TTF)_2[\text{Cu(NCS)}_2]\) shows several crossings at the Fermi level which should lead to metallic behaviour[38].
Figure 1.18: The Fermi surface derived from the band structure calculation starts as a cylinder bulging over the edge of the Brillouin zone in the \( Z \) direction as shown in (a). Separation of the bands where they cross on the \( Z-M \) boundary (b) results in separation into a sheet and a cylinder with corresponding one and two-dimensional electrical properties. The shaded region indicates a hole-like part of the Fermi surface[38, 39].
high magnetic field and at very low temperature. Conductivity fluctuations, depending on the applied field strength, are observed because the magnetic field forces electrons to move in orbits which are quantized. The quantization condition is a function of both the applied field \((B)\) and the particular electron orbits allowed by the band structure of the sample being studied. Theory predicts that a plot of conductivity as a function of \(1/B\) should give evenly spaced oscillations at intervals:

\[
\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{hcS},
\]

(1.1)

where \(e\) is the electron charge, \(c\) is the speed of light, and \(S\) is the area of an orbit in \(k\) space[9]. A full three-dimensional picture of the Fermi surface is obtained by varying the angle of the applied field. Shubnikov–de Haas measurements are generally difficult because quantization is only observable when the mean free path of the electron is comparable to or longer than the size of the orbit. Usually, this condition can only be met using a combination of the strongest available magnetic fields and sample temperatures well below 1 K. Under these conditions, it has been possible to obtain an accurate picture of the Fermi surfaces for many metals.

The experimental measurement of the Shubnikov–de Haas effect on \((BEDT-TTF)_2\,[Cu(NCS)_2]\) is shown in Figure 1.19 and confirms the presence of small closed loops on the Fermi surface. The period of the oscillation for field applied along the \(a\) axis corresponds to an area covering 18% of the Fermi surface, in agreement with the prediction of the tight binding model. In addition, Figure 1.20 shows that the observed oscillation period decreases with the angle of the applied field as \(\Delta(1/B) = (0.0015 \pm 0.0001) \cos \theta(T^{-1})\), where \(\theta\) is the angle between the field and the \(a\) axis. This agrees with the theoretical prediction of a cylindrical Fermi surface for which the closed loops have minimum area for the field applied along the \(a\) axis.
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Figure 1.19: At low temperatures and high magnetic field, the magnetoresistance shows Shubnikov–de Haas oscillations which confirm the theoretical prediction of a cylindrical Fermi surface with cross sectional area 18% of the total Brillouin zone[40].
Figure 1.20: Angular dependence of the observed Shubnikov–de Haas oscillations indicates a cylindrical Fermi surface oriented along the $a$ axis[41].
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Thermopower

Another confirmation of the general validity of the calculated band structure comes from the measurements of the thermopower. In these measurements, a temperature gradient across the sample induces a voltage which is measured. The thermopower, \( Q \), is defined as the factor relating the temperature change per length, \( \nabla T = dT/dx \), and the induced voltage, \( \varepsilon \):

\[
\varepsilon = Q \nabla T.
\]

A simple estimate of the thermopower based on a free-electron gas with a Fermi-Dirac distribution gives:

\[
Q = -\frac{\pi^2 k_b}{6e} \left( \frac{k_b T}{\varepsilon_f} \right),
\]

where \( k_b \) is Boltzmann's constant, \( e \) is the magnitude of the charge (the negative sign for the electron has already been included), \( T \) is the temperature, and \( \varepsilon_f \) is the Fermi energy[43]. This is a greatly simplified view and neglects important parameters such as the relaxation time, \( \tau \). A more complete picture becomes very complicated because \( \tau \) actually has energy dependence which is not completely understood. Therefore, the most important information that can be obtained from thermopower measurements is that \( Q \) will be negative for electron-like charge carriers and positive for hole-like charge carriers.

As shown in Figure 1.21, the thermopower of \((BEDT-TTF)_2[CU(NCS)_2]\) has the unusual property of being negative along the \( b \) direction and positive along the \( c \) direction for \((BEDT-TTF)_2[CU(NCS)_2]\)[42]. Considering the net charge of \(+\frac{1}{2}\) per \( ET \) molecule, a hole-like positive thermopower would be expected. An explanation for the unusual direction dependence can be found in the details of the calculated band structure. Electron-like thermopower along the \( b \) axis is due to the one-dimensional part of the band, while the hole-like thermopower along the \( c \) axis comes from the ellipse-like portion. It is well known that when a band is almost filled, as it is for these closed ellipse
portions, the electron transport will have hole-like properties [9].

**Magnetic Properties**

At temperatures above $T_c$, metallic or insulating sample behaviour can be distinguished by measurement of the magnetic susceptibility. Figure 1.22 shows susceptibilities for several types of systems [9]. For both paramagnetic insulators and a free electron gas, there is a Curie law $1/T$ dependence, but for metals and diamagnetic materials the susceptibility is nearly temperature independent. The difference between the almost constant susceptibility of metals and the $1/T$ response of the free electron gas was explained by Pauli using a band structure argument. Pauli’s calculation was based on the fact that for the metal all the electrons have fixed spin states except for those within a range $k_b T$ of the top of the Fermi surface. For these electrons, the linear temperature dependence of available states cancels with the $1/T$ electronic response. This is quite different from the cases of the paramagnetic insulator and free electron gas where each electron is free to choose its own spin direction [9, 43, 44].

Measurements of the $(B\text{EDT–TTF})_2[Cu(NCS)_2]$ magnetic susceptibility in Figure 1.23 show a nearly constant paramagnetic response between room temperature and 90 K and only a slight decrease between 90 K and 10 K [27, 32, 45]. After correction for the temperature independent diamagnetic contribution of the lattice, the observed response is in agreement with the Pauli paramagnetic response typical of metals. This indicates that the sample is not undergoing an insulator–metal transition at the 90 K dc resistivity maximum and is in agreement with the interpretation of the pressure dependent dc measurements.

Measurements of the magnetic properties of the sample below $T_c$ give important information about the superconducting state. For example, it is essential to observe magnetic flux exclusion (or the Meissner effect) to confirm the superconductivity. For
Figure 1.21: The thermopower measured for $\text{(BEDT-TTF)}_2\text{[Cu(NCS)}_2]$ has opposite sign along the $b$ and $c$ axes in the highly conducting plane. This indicates that electron-like charge carriers dominate the charge transfer along the $b$ direction and holes dominate in the $c$ direction. This is explained by the inset band structure for which the one-dimensional bands have electron-like properties and the cylindrical parts have hole-like behaviour[42].
Figure 1.22: Magnetic susceptibilities vary from nearly temperature independent in the case of metals and diamagnetic materials to $1/T$ behaviour typically seen in insulators[9].
Figure 1.23: Magnetic susceptibility of \((BEDT-TTF)_2[\text{Cu(NCS)}_2]\) is paramagnetic and nearly temperature independent above 10 K. Below 10 K the response becomes diamagnetic confirming the transition to the superconducting state[18].
(BEDT-TTF)$_2$[Cu(NCS)$_2$], a strong Meissner effect, above 80% perfect diamagnetism, is usually observed and is a good indicator of a bulk transition to the superconducting state [32, 46, 45, 47, 48].

Another fundamental property of the superconducting state is the critical field. Results of these measurements shown in Figure 1.24 demonstrate that (BEDT-TTF)$_2$[Cu(NCS)$_2$] is a type II superconductor with anisotropic critical fields. $H_{c1}$, the lower critical field, is of the order of 1 mT for a field applied along the poorly conducting $a$ axis and 5 mT for the field lying within the highly conducting plane [45]. These values are quite low compared to other superconductors. For example, lead alloys have $H_{c1}$ around 20 mT [9]. The upper critical field is also important for determining the usefulness of a material in practical applications. At $T=2$ K, observed values of $H_{c2}$ for (BEDT-TTF)$_2$[Cu(NCS)$_2$] are 20 T and 3 T for field orientations within and perpendicular to the highly conducting plane [48, 29]. This is the highest upper critical field ever observed for an organic superconductor. One very unusual and so far unexplained property is the upward curvature of $H_{c2}$ for the field along the $a$ axis. This is a substantial deviation from the linear temperature dependence of the Ginzburg-Landau theory which is observed for the other two directions and most other superconductors.

Detailed analysis of the magnetic response can also be used to obtain estimates of other superconducting state properties such as penetration depth, critical current and coherence length as well as normal state properties such as the density of states at the Fermi surface and transfer integrals. Coherence lengths and penetration depths obtained are $\xi_{b,c} : \xi_a = 182 \text{Å} : 9.6 \text{Å}$ and $\lambda_{b,c} : \lambda_a = 4000 \text{Å} : 15000 \text{Å}$ which are in reasonable agreement with the independently obtained $\mu^+SR$ results of $\xi = 135 \text{Å}$ and $\lambda = 9800 \text{Å}$ [30, 47, 49]. Measurement of the hysteresis of the magnetization curve at 4.9 K led to a critical current estimate of $J_c = 1060 \text{A/cm}^2$ [45]. The same author estimates the Fermi level density of states and the transfer integrals from the level of the susceptibility.
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Figure 1.24: The upper critical field of \((BEDT-TTF)_2[Cu(NCS)_2]\) is much higher for the field applied within the highly conducting plane. These upper critical fields are the highest observed for an organic superconductor\([48]\).
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at temperatures above 90 K. An assumption of Pauli paramagnetism gives \( N(E_f) \approx 7 \text{ eV}^{-1} \text{ spin}^{-1} \) per molecule, while a two-dimensional tight binding approximation gives the transfer integral value \( t = 0.04 \text{ eV} \). Published band structures have not yet included a density of states picture for comparison to this Pauli-paramagnet estimate but the general procedure is somewhat suspect since the derived transfer integral is several times smaller than other estimates based on the tight-binding calculation, temperature dependence of thermoelectric power, and optical spectra.

Heat Capacity and Tunnelling Measurements

Both heat capacity and tunnelling measurements can be used to estimate the binding energy of the superconducting electron pairs. However, the measurements on the organic superconductors do not show the dramatic features which are predicted by BCS theory and are observed in many superconducting materials. Because the results are not BCS-like, some very rough approximations have to be made in order to derive the superconducting electron binding energy.

Heat capacity for \((\text{BEDT-TTF})_2\text{[Cu(NCS)_2]}\) in the normal and superconducting states is shown in Figure 1.25. This data is qualitatively similar to that for classical BCS superconductors, with the superconducting heat capacity rising above the normal state value just below \( T_c \), and then dropping more rapidly to zero as the temperature goes to zero. However, the anomaly at \( T_c \), which would appear as a sharp discontinuity in a material such as aluminum, only appears as a broad hump in the \( ET \) measurement. Interpretation of heat capacity, to determine a value of the energy gap, depends on the size of the discontinuity at \( T_c \). Using the \( ET \) data, a rough estimation was made of the size of the discontinuity which would appear if the superconducting response concentrated rather than dispersed into the broad hump. However, there is a lot of uncertainty in the stated result, \( \Delta C/\gamma T_c > 2 \), which implies strong coupling superconductivity when
compared to the BCS-theory weak coupling limit of $\Delta C/\gamma T_c = 1.43$.

Tunnelling measurements have also been used in an effort to determine the superconducting pair binding energy for $(BEDT-TTF)_2[\text{Cu(NCS)}_2]$. For a BCS type material, the tunnelling current from the superconductor into a normal metal is zero until the potential required to break apart the superconducting electron pairs is reached. A typical spectrum for $(BEDT-TTF)_2[\text{Cu(NCS)}_2]$ is shown in Figure 1.26. There is some structure in the range of the predicted BCS gap energy but the shape of the curve is not at all similar to that which would be observed for an ideal superconductor. In addition, no clear change was observed at the superconducting transition temperature, and none of the important features could be reproduced using other crystals. Thus, the interpretation of this tunnelling data as implying a strong coupling limit, $2\Delta/k_B T_c = 4.5$ (compared to the BCS weak coupling value of 3.52), is not well founded.

Superconducting Penetration Depth

Magnetic field expulsion from the interior of a superconductor is one of the fundamental characteristics of the superconducting state. The only allowed internal field is one which decreases exponentially with the distance from the sample surface. The length scale associated with this exponential decrease is called the penetration depth, $\lambda$.

In a conventional BCS superconductor, the penetration depth has temperature dependence which can be approximated using the Gorter–Casimir law[49]:

$$\lambda(T) = \frac{\lambda(0)}{[1 - (T/T_c)^4]^{1/2}}.$$  \hspace{1cm} (1.4)

This equation shows that the penetration depth has a strong divergence at $T_c$, but goes to a constant value as the temperature approaches zero. Although Equation 1.4 is an empirical law, the approach of $\lambda$ to a constant value at low temperature is a characteristic expected for all conventional superconductors with isotropic gap functions.
Figure 1.25: Heat capacity of \((BEDT-TTF)_2[\text{Cu(NCS)}_2]\) displays a small effect at the superconducting transition. The BCS theory predicts a jump at \(T_c\), with the size of the discontinuity proportional to the superconducting energy gap, \(\Delta\). This data can only give a rough estimate for the gap energy, since the superconductivity produces only a broad hump just below \(T_c[51]\).
Figure 1.26: A tunnelling spectrum of \( (BEDT-TTF)_2[Cu(NCS)_2] \) shows structure in the region of the BCS electron pairing energy. However, those features which might be associated with the superconducting electrons do not show any clear change at the superconducting transition temperature and could not be reproduced using different samples[50].
Shown in Figure 1.27 is the magnetic penetration depth for \((BEDT-TTF)_2[Cu(N-CS)_2]\) as determined using both magnetic susceptibility and \(\mu^+SR\) measurements\(^{46, 49}\). At the lowest temperatures, the penetration depth derived from the magnetic susceptibility shows a power law dependence, indicating that the superconducting gap function is anisotropic with nodes on the Fermi surface. This power law temperature dependence is not observed in the \(\mu^+SR\) measurements in which the penetration depth seems to be approaching a constant value at low temperature. The presence of nodes in the gap function could be of great importance in relation to our effort to measure the superconducting gap optically. In any measurement which is dependent on the magnitude of the superconducting gap, the possibility of sensitivity to the minimum in the gap function must be considered.
Figure 1.27: Penetration depth for $(BEDT-TTF)_{2}[Cu(NCS)]_{2}$. (a) $\lambda(T)$ obtained from measurements of magnetic susceptibility[39]. (b) $\lambda(T)$ obtained using the $\mu^{+}SR$ technique[49].
1.2 Optical Spectroscopy

Infrared and far-infrared optical measurements are useful in helping to decide the important electrical processes taking place in materials. In metals, it is possible to see the frequency dependent response of the conduction electrons. For both metals and insulators there are broad features which reveal allowed energy levels near the Fermi surface in the electronic band structure. Lattice and molecular vibrations show up as smaller scale features in the spectra. In many cases these vibrational features are the expected normally active modes but in some special cases unusual coupling mechanisms can lead to observation of unexpected normally inactive vibrations. This section reviews some of the techniques used in making optical measurements and then presents some of the important results obtained for organic conductors and superconductors.

1.2.1 General Spectroscopic Techniques

Instrumentation

In the infrared and far-infrared part of the spectrum, optical measurements are usually made with spectrometers based on the Michelson interferometer [52]. With this type of instrument, a beamsplitter is used to send the light from a source along two paths which end with mirrors reflecting the beam back upon itself. Light from the two paths is recombined and then sent first to a sample chamber and then to a detector. Spectra are obtained by analysing the modulation of the signal when the path difference between the two arms of interferometer changes. A drawing of one of the first spectrometers used by Michelson in the late 1800's is shown in Figure 1.28 along with a schematic drawing labelling the essential components of a more modern instrument.

Power reflectivity $R$ and transmission $T$ are quantities commonly determined in optical measurements. A typical sample chamber used with a commercial interferometer
is shown in Figure 1.29(a). With this configuration, the quantity $R$ is obtained by exchanging the sample and a reference mirror at the focal point of the mirrors in the sample chamber. Transmission is measured with the sample situated at the middle of the chamber and the beam going straight through. Figure 1.29(b) shows the ray diagram of the Bruker 113V spectrometer which was used for the reflectivity measurements discussed in this thesis. Mirrors, with an arrangement similar to that shown in Figure 1.29, were inserted in one of the sample chambers.

To obtain an optical spectrum from this type of instrument requires some mathematical analysis. For a basic idea of how a spectrum is obtained, consider first what would happen if there was a purely monochromatic source producing light with wavenumber $\tilde{\nu} = 1/\lambda$ ($\lambda$ is the wavelength). As the path difference between the two arms of the interferometer changes, there is constructive or destructive interference as the recombining beams arrive in or out of phase. For source intensity, $S(\tilde{\nu})$, the intensity at the detector ($I$) as a function of the moving mirror position ($x$) will be:

$$I(x) = S(\tilde{\nu})[1 + \cos(2\pi \tilde{\nu} x)]. \quad (1.5)$$

For a non-monochromatic source, the intensity at the detector is a sum of many such sinusoidal components, each one having periodicity proportional to the wavelength and amplitude proportional to the source intensity at that frequency:

$$I(x) = \int_0^{\nu_{\text{max}}} S(\tilde{\nu})[1 + \cos(2\pi \tilde{\nu} x)]d\tilde{\nu}$$

$$= \frac{1}{2} I(0) + \int_0^{\nu_{\text{max}}} S(\tilde{\nu}) \cos(2\pi \tilde{\nu} x)d\tilde{\nu}. \quad (1.6)$$

Here, $I(0)$ is the integral (or signal) at zero path difference ($x = 0$). When the lengths of the paths along the two arms of the interferometer are the same, all frequencies recombine in phase and the detector measures a strong maximum. When the path difference
Figure 1.28: (a) The essential components of a Michelson interferometer. (A) Source. (B) Chopper. (C) Collimating mirror. (D) Beamsplitter. (E) Moving mirror. (F) Compensator. (G) Fixed mirror. (H) Focusing mirror. (I) Spectral filter. (J) Detector. (b) A drawing of one of Michelson’s early interferometers[52, 53].
Figure 1.29: (a) A schematic diagram of a commercial interferometer designed to measure both transmission and reflectivity. Reflectivity measurements require exchange of mirror M6 with the sample[53]. (b) Bruker 113V spectrometer[54].
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changes, the observed intensity is simply the sum of all the spectral components multiplied by their sinusoidal modulation frequencies. Performing a Fourier analysis of the measured signal as a function of path difference gives the optical spectrum:

\[ S(\nu) = \int_0^\infty [I(x) - I(\infty)] \cos(2\pi \nu x) dx. \]  

(1.7)

In the late 1800's when Michelson first developed this technique, he built a mechanical (but very elegant) spectral analyser to perform the Fourier transform. With modern computers, it is a simple matter to do the mathematics for a Fourier transform. For a measured interferogram with \( n \) points, application of Equation 1.7 requires summation of \( n^2 \) terms. The fast–Fourier–transform routine used in most modern computer calculations applies a mathematical technique called the Cooley–Tuckey algorithm[53]. Using this method reduces the number of steps to \( n \ln_2 n \), and significantly reduces the computation time since \( n \) is typically a number between 100 and 8000.

The interferometer has two advantages over grating spectrometers. Measuring a signal of the entire spectral intensity all the time gives these instruments a better signal to noise ratio (called the Fellgett or multiplex advantage) than a grating–type spectrometer. The problem with the grating instrument is that it separates the frequency elements and spends only a fraction of the total time measuring each. The second advantage of the interferometric technique is gained when measuring high resolution spectra and is known as the “Jacquinot” or “throughput” advantage. To increase resolution of a grating instrument requires a decrease in slit width, which also has the undesirable effect of reducing the signal. Thus, higher resolution requires an increase in not only the number of points, but also the measuring time for each. In contrast, for the interferometer an increase in resolution is obtained simply by increasing the travel distance of the moving mirror. Although this increases the number of points which are recorded, it does not involve any reduction in the measured signal amplitude since the solid angle...
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of light collected remains the same. The throughput advantage is reduced when using an interferometer for very high resolution measurements, since the size of the source aperture sets a limit on the ultimate resolution. Comparison of the power throughput for interferometers and grating instruments operated at similar resolution shows that the Jacquinot advantage is still significant[53].

Optical Relations

In measurements of the optical properties of a material, the fraction of light intensity reflected, absorbed or transmitted by the sample is determined as a function of photon energy. These three quantities are not independent because conservation of energy requires that the sum of reflected, absorbed and transmitted intensities must equal the incident intensity. This leads to the equation:

\[ R + A + T = 1.0. \]  

(1.8)

Particular characteristics of the sample being studied usually determine which of these three quantities will be measured. For almost all solid materials, the most convenient quantity to measure is the reflectivity. For single crystal organic conductors, transmission experiments are practically impossible due to a combination of high absorption coefficient and relatively thick samples. Thus, Equation 1.8 simplifies to:

\[ R + A = 1.0 \]  

(1.9)

for the organic metals, and the most convenient quantity, \( R \), is almost always measured.

Power reflectivity measurements do not by themselves provide a complete picture of the optical response of the material. What is missing is the phase difference between the incident and reflected radiation. This is included in the complex reflectivity which is
defined as the ratio of incident and reflected electric field amplitudes: \( \hat{E}_1 \) and \( \hat{E}_2 \):

\[
\hat{r} = \frac{\hat{E}_1}{\hat{E}_2} = \sqrt{R} e^{i\varphi_r}. \tag{1.10}
\]

The type of apparatus shown in Figure 1.29 determines the reflected intensity \( R \) but gives no information on the phase, \( \varphi_r \). It is desirable to know both \( \varphi_r \) and \( R \) because then all the other commonly used representations of the optical properties can be derived. For example, the real and imaginary parts of the index of refraction (\( n \) and \( k \)), the dielectric constants (\( \epsilon' \) and \( \epsilon'' \)), and the optical conductivity (\( \sigma_1 \) and \( \sigma_2 \)) can all be expressed as functions of \( R \) and \( \varphi_r \). Very often these other representations are useful in giving a clearer picture of the fundamental processes which contribute to the optical properties.

Several different procedures can be used to determine the phase of the reflected signal. Special instruments can be designed to allow either ellipsometric measurements (reflectivity as a function of incident angle) or asymmetric interferometry (the mirror in one arm of an interferometer is exchanged with the sample). For the small organic crystals which we work with it would be very difficult to apply either of these techniques. The other way to determine the phase is to analyse the reflectance using Kramers–Kronig relations. These equations can be applied to the real and imaginary parts of the optical response functions, \( \hat{n} = n + ik \), \( \hat{\epsilon} = \epsilon' + i\epsilon'' \) or \( \hat{r} = \sqrt{R} e^{i\varphi_r} \). The only requirement for exact solution is that the measured quantity must be known at all frequencies between 0 and \( \infty \). For example, the Kramers–Kronig relation used for calculating the phase from the reflectivity is\[55\]:

\[
\varphi_r(\omega) = \frac{\omega}{\pi} \int_{0}^{+\infty} \frac{\ln R(\omega')}{\omega^2 - \omega'^2} d\omega'. \tag{1.11}
\]

Experimentally measured values of \( R(\omega) \) invariably do not extend from \( \omega = 0 \rightarrow \infty \). In most cases, reasonable extrapolations can be made since the denominator of the integral makes \( R(\omega) \) unimportant for frequencies far from the region of interest. This
means that the Kramers-Kronig calculations can be applied with reasonable confidence even though $R$ is only known over a limited range.

Once both $R$ and $\varphi_r$ are known, it only requires straightforward algebra to derive other related optical parameters. For example, the most convenient description of the macroscopic optical response is in terms of the refractive index, $\hat{n} = n + ik$. For normally incident radiation on a surface in a vacuum, the equations relating $n$ and $k$ to measured values of $R$ and $\varphi_r$ are:

$$ R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} $$

$$ \varphi_r = \tan^{-1}\left(\frac{2k}{n^2 + k^2 - 1}\right) $$

or conversely:

$$ n = \frac{1 - R}{1 + R - 2\sqrt{R}\cos \varphi_r} $$

$$ k = \frac{2\sqrt{R}\sin \varphi_r}{1 + R - 2\sqrt{R}\cos \varphi_r} $$

For non-normally incident light, the reflectivity in terms of $n$ and $k$ becomes a complicated function of both the angle of incidence and the polarization[55].

The other important quantities for describing spectroscopic response on a more fundamental level are the dielectric constant $\varepsilon$, and the conductivity $\sigma$. In terms of the refractive index, the dielectric constant is given by:

$$ \varepsilon = \varepsilon' + i\varepsilon'' = \hat{n}^2 = (n + ik)^2 $$

Equating real and imaginary parts gives $\varepsilon'$ and $\varepsilon''$ in terms of $n$ and $k$ (which are already known in terms of $R$ and $\varphi_r$):

$$ \varepsilon' = n^2 - k^2 $$

$$ \varepsilon'' = 2nk $$
Inverting these equations and putting in the frequency dependence explicitly in terms of the common spectroscopic units, \( \nu = 1/\lambda \), gives:

\[
\begin{align*}
\epsilon'(P) + \frac{y}{\epsilon'(P)} & + \epsilon''(P) \\
\mu & = \frac{\hbar}{m} + Je^{\nu}(py + \epsilon''(P)^2) \\
\epsilon'(P) + \sqrt{\epsilon'(P)^2 + \epsilon''(P)^2} \\
k(\nu) & = \sqrt{\frac{1}{2} - \epsilon'(P) + \sqrt{\epsilon'(P)^2 + \epsilon''(P)^2}}.
\end{align*}
\] (1.19) (1.20)

Equations relating the complex dielectric function to the reflectivity turn out to be relatively simple:

\[
\hat{\epsilon}(\nu) = \frac{[1 + \hat{R}(\nu)]^2}{[1 - \hat{R}(\nu)]^2} = \frac{[1 + \|R(\nu)\|^{1/2}e^{i\phi_R(\nu)}]^2}{[1 - \|R(\nu)\|^{1/2}e^{i\phi_R(\nu)}]^2}.
\] (1.21)

Complex conductivity and dielectric functions are related using the equation[55]:

\[
\sigma = \sigma_r + i\sigma_i = i\omega\epsilon_0(1 - \hat{\epsilon}),
\] (1.22)

where \( \epsilon_0 = 8.854 \times 10^{-12} C^2/Nm^2 \) is the permittivity of free space. The real part of the optical conductivity is one of the most commonly used optical properties because at low frequency it can be compared to results of dc resistance measurements. Inserting the numerical value for \( \epsilon_0 \) and converting the frequency to wavenumbers gives:

\[
\sigma_r(\tilde{\nu}) = \frac{n(\tilde{\nu})k(\tilde{\nu})\tilde{\nu}}{30} = \frac{\epsilon''(\tilde{\nu})\tilde{\nu}}{60},
\] (1.23)

where a value of \( \tilde{\nu} \) measured in \( cm^{-1} \) gives the conductivity in units of \( \Omega cm^{-1} \).

After presenting all of these formulas, it might be useful to explain why it is usually desirable to convert from the measured reflectivity \( R \) to one of these other quantities. The index of refraction, \( \hat{n} \), is best for describing macroscopic properties of the medium. For example, it is fairly easy to determine the reflectivity from \( \hat{n} \) using Equation 1.12 or the more complicated formulas which are applied for non—normal angles of incidence. In
a dielectric medium, the real and imaginary parts of \( \hat{n} \) are related to more fundamental characteristics, the velocity of light propagation and the absorption coefficient. In one-dimension, the amplitude of an electric field propagating into a dielectric material with index \( \hat{n} \) is given by the equation:

\[
E = E_0 e^{(-i\omega k)} = E_0 e^{-i\omega k} e^{-\frac{\omega k}{\epsilon}},
\]

(1.24)

where \( E_0 \) is the electric field amplitude at the surface of the dielectric, \( E \) is the field amplitude at the position \( x \), \( \omega \) is the angular frequency of the light and \( c \) is the speed of light in a vacuum. It is clear that \( c/n \) is the effective speed of electric field propagation and \( \omega k/c \) is proportional to the dielectric absorption coefficient, \( \alpha \). Taking into account the fact that \( \alpha \) describes attenuation of intensity rather than amplitude, the relationship between \( k \) and \( \alpha \) is:

\[
\frac{\alpha}{2} \frac{\omega k}{c} = 2\pi \bar{v} k.
\]

(1.25)

Drude–Lorentz Model

While \( \hat{n} \) is convenient for analysis of macroscopic properties, the dielectric function \( \epsilon \) is most useful in describing the microscopic response of the medium. For an external field \( E \), the factor \( \epsilon \) is used to convert to the internal field \( D \) seen inside the dielectric medium:

\[
D = \epsilon E.
\]

(1.26)

One of the simple models for the response of microscopic charges to an applied field is the Drude–Lorentz theory. In this model, electrons are treated as damped oscillators with resonant frequency \( \omega_0 \), and damping \( \gamma \). For a metal with several different response frequencies with different strengths and dampings, the Drude–Lorentz dielectric function is[16, 55]:

\[
\epsilon - \epsilon_c = \sum_i \frac{\omega_{pi}^2}{\omega_0^2 - \omega^2 - i\gamma_i\omega}.
\]

(1.27)
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Separating real and imaginary parts gives:

\[
\epsilon' = \epsilon_c + \sum_i \frac{\omega_{pi}^2 (\omega_i^2 - \omega^2)}{\omega_i^2 - \omega^2 + (\gamma_i \omega)^2}
\]  \hspace{1cm} (1.28)

and:

\[
\epsilon'' = \sum_i \frac{\omega_{pi}^2 \gamma_i \omega}{\omega_i^2 - \omega^2 + (\gamma_i \omega)^2}.
\]  \hspace{1cm} (1.29)

For this model, the various contributions to the total response add linearly into \( \epsilon \) and are easily separated in comparison to the convoluted mixture which would appear in the power reflectivity, \( R \).

Combining Equations 1.23 and 1.29 and converting to frequency in wavenumbers gives the real part of the optical conductivity:

\[
\sigma_r(\tilde{\nu}) = \frac{1}{60} \sum_i \frac{\omega_{pi}^2 \gamma_i \tilde{\nu}^2}{\omega_i^2 - \tilde{\nu}^2 + (\gamma_i \tilde{\nu})^2}.
\]  \hspace{1cm} (1.30)

For this Drude–Lorentz model, the real part of the conductivity at \( \tilde{\nu} = 0 \) is always zero unless a term is included with \( \omega_{0i}^2 = 0 \). The contribution from such a term is called a Drude–like conductivity, having a peak at \( \omega = 0 \) with half width \( \gamma \):

\[
\sigma(\tilde{\nu}) = \frac{1}{60} \frac{\omega_p^2 \gamma}{\omega^2 + \gamma^2}.
\]  \hspace{1cm} (1.31)

In this case, the quantity \( \omega_p \) is called the plasma frequency and a simple Drude model gives (in SI units)[9]:

\[
\omega_p^2 = \frac{n e^2}{\epsilon_0 m^*},
\]  \hspace{1cm} (1.32)

where \( \epsilon_0 = 8.854 \times 10^{-12} \frac{C^2}{Nm^2} \) gives \( \omega_p \) in \( sec^{-1} \). This type of frequency dependent response is observed in many metals, especially at low frequencies. Keeping both the real and imaginary parts of \( \epsilon \) and taking a low frequency limit gives the Hagan–Rubens relation which provides a good fit with the data for many materials:

\[
A = 1 - R \approx 2 \sqrt{\frac{2\epsilon_0 \omega}{\sigma_{dc}}} = 2 \sqrt{\frac{\tilde{\nu}}{30\sigma_{dc}}}. \hspace{1cm} (1.33)
\]
Figure 1.30: Calculated reflectivity from a Drude model. At low frequency, $1 - R$ is proportional to $\omega^{1/2}$ as given by the Hagen–Rubens relation. The drop in reflectivity occurs at a frequency given approximately by $\omega_p$. 

$\omega_p = 5000 \text{ cm}^{-1}$ 
$\gamma = 210 \text{ cm}^{-1}$
With the Hagen–Rubens equation in this form, the frequency measured in wavenumbers and dc conductivity in \((\Omega \text{cm})^{-1}\) gives the absolute absorptance.

A plot of the reflectivity which results from a Drude type conductivity is shown in Figure 1.30. Parameters used in this calculation have been chosen to give both a general spectral shape and a dc conductivity close to that observed in many of the organic conductors. The important features are the sharp drop in \(R\) at a frequency of approximately \(\omega_p\) and the agreement with the Hagen–Rubens law in the low frequency region below \(\gamma\).

### 1.2.2 Infrared Optical Properties of Organic Conductors

Organic conductors are not ideal materials for spectroscopic measurements. The perfect sample would be indestructible and have a large mirror–like surface. Organic conductors do not have either of these characteristics. They are usually very small, come with multiple crystals bonded together, and are very easily damaged by both handling and thermal cycling. The small size of the reflecting surface creates particular difficulties for far–infrared measurements. In this region, sources are weak, long wavelengths are diffracted out of the beam, and metallic properties bring the reflectance up to close to 1.0.

Despite the difficulties associated with working on organic conductors, infrared reflectance measurements have now been conducted on many of the Bechgaard \(TMTSF\) and \(BEDT–TTF\) based materials. Several common features are beginning to emerge including the overall shape and specific molecular vibrations. A simple interpretation of the results is often possible in terms of a Drude–Lorentz model.

Mid–infrared reflectivity measurements for several of the metallic Bechgaard and \(ET\) organic conductors are shown in Figures 1.31 and 1.32. For light polarized along the
highly conducting axis, both the TMTSF and ET salts have a reflectivity which is relatively high in the far and mid-infrared and then drops steeply to a minimum somewhere between 4000 cm\(^{-1}\) to 7000 cm\(^{-1}\). The position of the minimum varies considerably with different materials, temperature, and the polarization of the light. The temperature dependent increase in the reflectivity, shown in Figure 1.32, is associated with the increasing conductivity of these ET salts at lower temperatures. This type of temperature dependent reflectivity, where most of the increase is confined to the lower frequency region, is common in the organic metals.

In early work, reflectivity spectra were interpreted in terms of the calculated Drude response such as that shown in Figure 1.30. Similarities between these measured spectra and this type of calculation are clear. There is relatively high and constant reflectivity at low frequencies and then a rapid drop to a value very close to zero in the mid-infrared. A more detailed comparison of the data with the theory shows that a reasonable fit can be obtained using the Drude model only in the region of the reflectivity minimum. In the low frequency region however, the resulting calculated reflectivity becomes much too high. Initially, it was speculated that a depressed reflectivity might result from a poorly conducting or contaminated sample surface. The measurements are reproducible however, and recent scanning tunnelling microscope images show that the surfaces of good samples are clean and defect free.

A better understanding of the spectrum was obtained when Kramers-Kronig calculations were performed. In plots of the optical conductivity, the difference between a purely Drude-like response and the measured spectra becomes much clearer. For example, Figure 1.33 shows the optical conductivities obtained from the reflectances shown in Figure 1.32. At room temperature, the spectrum is dominated by a broad hump which loses some strength when the sample becomes a better conductor at lower temperature. The region in which the metallic behaviour is observed actually lies below about
Figure 1.31: Reflectivity of several TMTTF and TMTSF organic conductors with light polarization parallel to the conducting stacks[56].
Figure 1.32: Reflectivity of two typical ET salts having a stacked molecular arrangement. (a) Light polarized along the stacks. (b) Light polarized perpendicular to the stacks[57].
1000 cm$^{-1}$. Clearly, a single Drude–like term is not responsible for the overall shape of either the reflectivity or the conductivity. In particular, the steep decrease and minimum at about 5000 cm$^{-1}$ should not be associated with the plasma frequency, $\omega_p$, in the Drude formula.

In many cases, a reasonably good fit with the the observed spectra of organic conductors can be obtained using the relatively simple Drude–Lorentz model[16]. A broad Lorentzian oscillator is used to give the mid–infrared hump, narrower Lorentzians simulate the phonons, and a Drude term models the metallic behaviour. When the system becomes more complicated, as with the highly one–dimensional materials which undergo Peierls transitions, the theoretical models become much more difficult and the calculations required for comparison with data are quite complex[116, 59, 60].

Phonon modes associated with molecular vibrations are observed superimposed on the reflectivity in the region below 2000 cm$^{-1}$. For the organic $BEDT-TTF$ and $TMTSF$ molecules, detailed group theory calculations have been performed to determine the allowed modes of vibration, their frequencies, and the isotope shifts for substitution of the hydrogen atoms with deuterium. These calculations apply to an isolated molecule but can be compared to the optical measurements on the solid materials. This allows assignment of most of the observed features to specific vibrational modes. Reliable identification involves measurements of both protonated and deuterated samples at both room temperature and low temperature. The low temperature spectra are important because some of the vibrations, which are broad and overlapping at room temperature, become narrower and are resolved when the temperature is lowered.

The few diagrams included in this section are meant to provide only a brief introduction to the optical properties of the organic conductors. Much more detailed spectra are upcoming in this thesis. Several other groups have also been actively involved in this field. Work with the Bechgaard salts was conducted mainly in Europe and North
Figure 1.33: The mid-infrared conductivity of ET conductors does not have a Drude-like shape. Metallic behaviour is only associated with the lower frequency region where the conductivity increases with decreasing temperature[57].
Chapter 1. Introduction

American [59, 61, 62, 63, 64] while the research effort on the ET based compounds has extended to include many Soviet and Japanese scientists [65, 66, 67, 68, 69, 70, 71, 72].

1.2.3 Superconductors

Far-infrared optical measurements have played an important role in the characterization and theoretical analysis of all types of superconductors. Some of the earliest predictions of the BCS theory of superconductivity were verified by optical transmission measurements on thin films of superconducting lead and tin [73, 74]. This early success has been followed by steady improvements in experimental technique which have allowed verification of more detailed calculations which remove many of the simplifying approximations of the original BCS derivation. However, the BCS theory remains at the heart of explaining the superconducting state.

BCS Optical Response

Bardeen, Cooper, and Schrieffer presented the first theoretical model to explain superconductivity on a microscopic level. Their theory shows how electron–phonon interactions can lead to a net attraction and pairing of electrons near the Fermi surface. At very low temperatures, where most of the random thermal motion of the lattice is frozen, this attracting force between electrons is strong enough to overcome the Coulomb repulsion. The resulting state encourages formation of correlated electrons pairs with total spin zero which allows Boson–like condensation into a single energy state. The unusual electrical and magnetic characteristics of the superconducting state result from the collective motion of these paired electrons. Other properties, such as heat capacity and optical absorption, are more easily understood as resulting from the gap in energy between paired and unpaired electrons at the Fermi energy.
One of the most important features of the superconducting state is that electrons can move through the solid with absolutely no scattering. These electrons respond in a unique way to optical radiation. While the normal electrons can absorb light and transfer the energy to the lattice through collisions, the superconducting electrons have no mechanism through which to absorb energy. Thus, unless a photon has enough energy to break apart a pair of electrons, absorption does not occur. At absolute zero, condensation of all the electrons into the superconducting state leads to zero absorptance and perfect reflectivity in the energy range below the electron binding energy, called $2\Delta$.

According to the original BCS theory, the energy $2\Delta$ at $T=0$ K should be related to the transition temperature, $T_c$, by the equation:

$$2\Delta_0 = 3.5k_bT_c,$$  \hspace{1cm} (1.34)

where $k_b$ is Boltzmann's constant. For example, a superconductor with a transition temperature of 10.4 K has a gap energy lying in the far-infrared at 25 cm$^{-1}$. As the temperature increases and approaches $T_c$, the measured gap does not remain constant but decreases to zero as shown in Figure 1.34. From this diagram, it can be seen that a fully developed gap requires a temperature of about $0.5T_c$.

Two measured optical spectra which show effects of the superconducting transition follow. For the ceramic superconductor $BaPb_{1-x}Bi_xO_3$ with $T_c = 9.5$ K, there is a dramatic increase in the far-infrared reflectivity below the BCS energy $2\Delta$ as shown in Figure 1.35. The shape of the reflectance ratio, $R_s/R_n$, is in agreement with a standard BCS calculation with a gap energy given by Equation 1.34. A far-infrared measurement of the absorptance of superconducting lead is shown in Figure 1.36. For the spectrum measured at a temperature far below $T_c$, the absorptance drops to zero in the far-infrared region below the energy $2\Delta$[76].
Figure 1.34: Measured energy gaps decrease as $T$ approaches $T_c$, in agreement with the BCS theory[9].
Figure 1.35: Far-infrared reflectivity of BaPb1 - xBi2O3 in the superconducting and normal states shows evidence of the superconducting transition. This sample has $T_c \approx 9.5$ K, and the ratio of superconducting and normal state reflectivities shows a difference in the far-infrared region in agreement with the BCS prediction. The upper curve shows the ratio of the spectra measured at 3 K and 10 K, while in the lower curve, the normal state properties established by application of a magnetic field[75].
Figure 1.36: The absorption of superconducting lead drops to zero for photon energies between 0 and $2\Delta[76]$. 
Strong/Weak Coupling

The relationship given in Equation 1.34 between the gap energy and the superconducting transition temperature is called the weak coupling limit. In deriving this formula, the phonon spectrum was approximated as being flat and frequency independent. In many cases, this is not a good approximation because specific low-frequency phonons enhance the electron-phonon interaction. When such low frequency phonons are important, the gap in the optical spectrum can appear at an energy $2\Delta > 3.5k_B T_c$ and the sample is called a strong coupling superconductor. Many materials have this characteristic, including the lead sample illustrated in Figure 1.36 for which the drop to zero absorptance occurs at the energy corresponding to $2\Delta \approx 4.3k_B T_c$. In this way, optical measurements have been used to measure the superconducting electron pair binding energies for many superconductors. The most sensitive measurements on the strongly coupled superconductors also show features corresponding to the important phonon modes in the energy region near $2\Delta$ which are directly responsible for the strong coupling mechanism[76, 77, 78].

For organic superconductors, the issue of the superconducting mechanism is still the subject of some debate. Gap estimates based on specific heat and tunnelling measurements suggest the possibility of a strong coupling mechanism with $2\Delta/k_B T_c \approx 4$–4.5, but these claims are strongly dependent on choices made in interpretation of the data[51, 50, 79]. An optical measurement of the superconducting gap could resolve the issue.

Cases in Which the Gap May be Difficult to Observe

The simplest BCS model predicts a rise to 100% reflectivity and zero absorptance at $T = 0$ for photons below the energy $2\Delta$. There are several cases where this change might be hard to detect experimentally or might occur at an energy other than that predicted
Chapter 1. Introduction

by Equation 1.34.

One case where the effects of a superconducting transition would be hard to detect optically is that in which the superconductor is in the clean limit. A straightforward BCS model can be used to predict the optical properties of superconductors in either a clean or dirty limit. The dirty limit is characterized by a high scattering rate for the conduction electrons, making the normal state Drude conductivity peak wider than the superconducting binding energy, $2\Delta$. In the clean limit, the scattering rate is low and the Drude conductivity peak is much narrower than $2\Delta$. In both cases, the basic BCS prediction of perfect reflectivity and zero absorption at $T = 0$ remains unchanged. For the clean limit superconductor however, the normal state electrons absorb a negligible amount at the energy $2\Delta$ and the drop to identically zero absorptance has very little impact on the optical properties. Many of the high-$T_c$ superconductors are believed to be in this limit, exhibiting such a small change in $R$ at $2\Delta$ that it is completely overwhelmed by other absorption processes such as phonons and charge transfer bands[80, 81].

So far, this section has concentrated on the zero temperature limit for which the superconducting optical response is particularly simple. When the temperature is non-zero, not only does the gap energy decrease as shown in Figure 1.34, but the absorption is no longer identically zero below $2\Delta$. This means that the difference between superconducting and normal state responses becomes somewhat reduced as shown in Figure 1.37 for measurements on superconducting aluminum.

There are several other circumstances in which the size of the gap could become zero while the sample retains superconducting characteristics. For temperatures close to but below $T_c$, materials in which there are magnetic impurities can simultaneously display no gap at the Fermi surface and superconducting characteristics[83]. It is not necessary to explain this particular situation in much depth here since the organic superconductors do not have the magnetic impurities which could lead to this type of behaviour.
Figure 1.37: Surface resistance measurements for aluminum show both a change in gap energy as a function of temperature and non-zero absorptance at $T \neq 0$[82].
It is also possible to have superconductors in which the size of the energy gap is anisotropic. Even for some of the conventional metals such as zinc or tin, the gap can vary as much as 30% along different directions in reciprocal space[84, 85]. Considering the Fermi surface of the organic materials, an even stronger anisotropy might be expected. In this case, it is possible to have nodes at which the gap function is zero at some points on the Fermi surface. The simplest prediction is that averaging the gap over all the directions should still give the BCS value of $2\Delta = 3.5k_B T_c$. 
Chapter 2

Bolometric Measurements

The bolometric technique provides one of the most sensitive ways of measuring absorption of infrared and far-infrared radiation. Of particular interest is the way in which it has been successfully used to measure the superconducting gap and phonon features of the lead superconductor as shown in Figure 1.36. In measurements looking for the effects of a superconducting transition, there is an advantage in measuring $A$ rather than $R$. Reflectivity measurements are relatively insensitive because the sample is already a highly reflecting metal in the normal state, and therefore, the change to perfect reflectivity can be only a fraction of a percent. However, the absorption signal, which is proportional to $1 - R$, should show a relatively large change. Absorption due to conventionally paired BCS conduction electrons should drop to zero for optical energies between 0 and $2\Delta$ when the temperature is well below $T_c$.

2.1 Bolometric Technique

In bolometric measurements, optical power absorption is measured using a sensitive thermometer to determine the heating effect on the sample. This type of technique was used as early as the year 1800, when the existence of infrared radiation was discovered using a glass bulb thermometer[86, 87]. The first electrical bolometer was made in 1880 using metallic platinum as the thermometer in a Wheatstone bridge measuring circuit. Recently, semiconducting thermometers have become more common because they have an exponentially rising resistance at low temperature. This gives these thermometers
Chapter 2. Bolometric Measurements

Figure 2.1: In bolometric measurements, absorption of incident light produces a temperature increase which is measured with a thermometer. This schematic drawing shows roughly how the absorptance of a sample can be measured using an electrical thermometer with temperature dependent resistance.

great sensitivity at low temperature but places some restriction on the operating range. Typical operating temperatures are limited to within a few degrees of the boiling point of liquid \( ^4\text{He} \) at 4.2 K.

A diagram of a bolometric detector is shown in Figure 2.1. The temperature rises when the sample absorbs radiation and, for these experiments, the increase was measured using a small doped silicon thermometer mounted on the back. A small bias current is passed through the thermometer and the radiation is chopped so that the thermometer signal can be fed into a lock-in amplifier.

A major problem in constructing a bolometric detector is maintaining a compromise between high sensitivity and a reasonable response time constant. The time constant is determined by the ratio between heat capacity, \( C \), and thermal conductivity between the
Chapter 2. Bolometric Measurements

thermometer and the mount, $G$:

$$\tau = \frac{C}{G}. \tag{2.1}$$

Maximum sensitivity requires minimization of the thermal conductivity, but this could quickly lead to an excessive time constant if a corresponding effort was not made to keep the heat capacity low. One common way of obtaining a relatively large absorbing area while minimizing the total heat capacity is to make a composite bolometer. A material with the lowest possible heat capacity is chosen to make the absorbing substrate. All other components, including the semiconducting thermometer, are kept as small as possible. The other way to minimize heat capacity is to operate the bolometer at low temperature, since contributions to heat capacity from the conduction electron gas and lattice vibrations decrease as $T$ and $T^3$ respectively. To take advantage of the reduced heat capacity at low temperature, all of the most sensitive bolometric detectors operate at cryogenic temperatures.

Absorbing substrates for composite bolometric detectors are usually made from sapphire wafers. Diamond has a lower heat capacity than any other solid but does not come in a form, or at a price, suitable for construction of bolometers. Sapphire is the next best substance in terms of heat capacity, and it is readily available in the form of thin wafers suitable for use as bolometer absorbing substrates. Although sapphire itself does not absorb well in the far-infrared region below $350 \text{ cm}^{-1}$, thin metal films evaporated onto the surface can be used to give relatively frequency independent absorption characteristics. Film thickness is typically about $10^{-5} \text{ cm}$, but for this type of detector even this small amount is enough to contribute substantially to the total heat capacity. Table 2.1 lists some of the materials used in making a composite bolometer and their contributions to the heat capacity. The heat capacity of a normal size ($BEDT-TTF)_2[Cu(NCS)_2]$ crystal is also included for comparison[88].
Table 2.1: Estimates for heat capacities of various materials used in construction of a composite bolometer[89, 90, 91]. Assuming an operating temperature of approximately 5 K, the final column shows only the larger of the terms proportional to $T$ or $T^3$.

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Capacity (μJ/cm$^3$K)</th>
<th>Volume (cm$^3$)</th>
<th>Contribution (J/K) $\times 10^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Thermometer[90]</td>
<td>$0.47T^3$</td>
<td>$0.033 \times 0.033 \times 0.05$</td>
<td>$0.25T^3$</td>
</tr>
<tr>
<td>Sapphire[89]</td>
<td>$0.4T^3$</td>
<td>$0.4 \times 0.4 \times 0.0025$</td>
<td>$1.6T^3$</td>
</tr>
<tr>
<td>Metal (Bismuth) film[90]</td>
<td>$3.2T + 56T^3$</td>
<td>$0.4 \times 0.4 \times 10^{-5}$</td>
<td>$0.9T^3$</td>
</tr>
<tr>
<td>Gold Electrical Leads[90]</td>
<td>$72.4T + 42.3T^3$</td>
<td>$0.6 \times \pi \times (0.00125)^2$</td>
<td>$1.2T^3$</td>
</tr>
<tr>
<td>Brass Leads[89, 90]</td>
<td>$\approx 500T + 3T^3$</td>
<td>$0.6 \times \pi \times (0.00125)^2$</td>
<td>$15T$</td>
</tr>
<tr>
<td>Stainless Steel Leads[91]</td>
<td>$3000T + 2.5T^3$</td>
<td>$0.6 \times \pi \times (0.00125)^2$</td>
<td>$90T$</td>
</tr>
<tr>
<td>BEDT-TTF Crystal[88]</td>
<td>$25T + 8.5T^3$</td>
<td>$0.1 \times 0.2 \times 0.01$</td>
<td>$17.2T^3$</td>
</tr>
</tbody>
</table>

It is clear from Table 2.1 that composite bolometers made using organic ET crystals as absorbers will have a heat capacity completely dominated by the sample. Some sensitivity must be sacrificed in order to obtain a signal at a reasonable chopping frequency of about 5 Hz, especially since it is necessary to measure spectra both above and below the superconducting temperature of $T_c=10.4$ K. Thus, the requirements for the thermal link to the sample mount are quite different for an organic composite bolometer than for the most sensitive detectors which have very low heat capacity and operate at temperatures below 1 K.

The dominant thermal link between the thermometer and the mount is almost always designed to be through the thermometer electrical leads. At cryogenic temperatures, alloys have much lower thermal conductivities than pure metals and therefore sensitive detectors are usually made using brass or stainless steel thermometer leads. For a bolometer with exceedingly low heat capacity, an even poorer thermal conductor can be found in a superconducting metal such as aluminum[92]. For bolometric measurements using organic crystals, the high heat capacity of the sample makes it necessary to increase the thermal connection to the cryostat by using highly conducting gold or
copper thermometer leads. These materials have thermal conductivities about 100 times higher than that of an alloy. Materials with much lower thermal conductivity such as very fine nylon or glass fibers are sometimes used to provide additional supports for the absorbing bolometer substrate.

2.1.1 Bolometer Sensitivity Calculation

After a bolometer has been assembled, it is important to characterize the sensitivity and response time constant. The time constant is determined by measuring the signal as a function of the chopping frequency of incident radiation. Sensitivity is more difficult to determine and is accomplished by measuring the load curve (voltage versus current) characteristics for the detector[93].

A typical biasing circuit for a bolometric measurement is shown in Figure 2.2. A battery or low noise dc power supply provides a constant voltage and, in the usual case where $R_{\text{load}} \gg R_{\text{bol}}$, drives a nearly constant current through the circuit. Using the dc power supply allows variation of the current for measurement of a load curve, an example of which is shown in Figure 2.3. As the current increases, the electrical power dissipated in the thermometer causes a rise in temperature. For the semiconducting thermometers used in these experiments, decreasing thermometer resistance with increasing temperature causes the upward curvature of the $E$ (voltage) versus $I$ (current) plot.

Analysis of the load curve to derive sensitivity is only possible if electrical and radiative power inputs have the same effect on thermometer temperature. Ensuring that this is the case requires having the only thermal path from the absorber to the mount passing through the thermometer leads as shown in Figure 2.1. When this condition is met, then radiative heat absorbed by the substrate must be conducted away through the thermometer and the induced temperature rise is equivalent to that resulting from direct electrical heating of the thermometer. It is easy to imagine the opposite extreme,
Current, $I$

Battery $E_{batt}$

$R_{load}$ (Load resistance)

$R_{bol}$, $E_{bol}$ (Bolometer)

Figure 2.2: A series circuit, containing a battery, a load resistor, and the bolometer, is used for measurements. The bolometer resistance changes with radiative heating and the resulting voltage change is amplified and measured.

where the main thermal connection to the mount is through the substrate. In this case, the thermometer temperature change resulting from electrical power input will be larger than that due to radiative power input, especially if the thermal connection between thermometer and substrate is poor. Thus, determination of sensitivity from load curve analysis requires construction of the bolometer in such a way that the only important thermal link to the mount is through the thermometer leads.

For analysis of the load curve sensitivity, a conversion is first required from voltage versus current to resistance as a function of power input. For a small change in electrical power input, the change in bolometer resistance is given in terms of the load curve voltage and current parameters by[93]:

$$\frac{dR_{bol}}{dP} = \frac{d(E/I)}{d(EI)} = I^2 \left[ \frac{Z - R_{bol}}{Z + R_{bol}} \right],$$  \hspace{1cm} (2.2)

where $Z = (dE/dI)$ is the slope of the measured load curve.
Figure 2.3: The measured load curve for a bolometer made with a semiconducting thermometer has curvature resulting from decreasing resistance with increasing temperature. This particular curve comes from the specification sheets for a commercially produced detector[94].
Chapter 2. Bolometric Measurements

The next step in the analysis is to equate the change in bolometer resistance resulting from absorption of radiation with the corresponding load curve heating. For a bolometer constructed as outlined above, the two forms of heat input should result in exactly the same change in bolometer resistance. For radiative heating, the calculation requires accounting for both the change in radiative power, $Q$, and the smaller change in electrical heating due to the change in bolometer resistance:

\[
\left(\frac{dP}{dR_{bol}}\right)_{\text{Load Curve}} = \left.\frac{d(EL + Q)}{dR_{bol}}\right|_{E_{\text{load}}, E_{\text{batt}} = \text{Const}}. 
\] (2.3)

For the biasing circuit as shown in Figure 2.2, the constraints on the right hand side of the equation are that the load resistance, $R_{\text{load}}$, and the battery voltage, $E_{\text{batt}}$, are constant. Using Equation 2.3 for the left side, and analysing the right side with the required parameters kept constant gives:

\[
\frac{dE}{dQ} = S = \frac{R_{\text{load}}(Z - R_{bol})}{2R_{bol}I(Z + R_{\text{load}})},
\] (2.4)

where $S$ is the sensitivity of the bolometer with units of $\frac{\text{Volts}}{\text{Watt}}[93]$. From Equation 2.4, it can be seen that the sensitivity will be poor with very high currents. With low current, sensitivity also decreases because there is almost no electrical heating of the thermometer, resulting in $Z \approx R_{bol}$. At higher currents, the sensitivity drops due to the $1/I$ dependence. Sensitivity will be a maximum at some intermediate current, to be determined by inserting the data points from a measured load curve in Equation 2.4.

2.1.2 Contributions to Bolometer Noise

Detector noise is most conveniently discussed in terms of the noise equivalent power or NEP. The NEP is the amount of absorbed power which would give the bolometer a signal to noise ratio of unity. For a bolometer operating at temperature $T$, the following
terms contribute to the measured noise:\[89\]:

\[
(NEP)^2 = 2k_bT_B \varepsilon_P + 4k_bT^2 G + \frac{4k_bTR}{S^2} + \frac{4k_bT_L R_L}{S^2} \left( \frac{R}{R_L + R} \right)^2 + \frac{NI^2R^2}{\omega S^2} + \text{amplifier noise.}
\]  

Fluctuations of the background radiation originating with source temperature \(T_B\) gives the first term, where \(\varepsilon_P\) is the absorbed power and \(k_b\) is the Boltzmann constant. Next comes a term resulting from random fluctuations in the thermal conductance, \(G\), of energy between the sample and the mount. The following two terms result from Johnson noise of the bolometer resistance at temperature \(T\) and the load resistance at temperature \(T_L\), and are inversely proportional to the detector sensitivity, \(S\). The last term comes from the current noise of the detector and is scaled using the dimensionless constant, \(N\). Current noise can be distinguished from other terms in this equation by the proportionality to detector current and the \(1/\omega\) frequency dependence.

Table 2.2 shows the calculated noise contributions for one of the composite bolometers constructed for measuring the absorption of the organic superconductor, \((BEDT-TTF)_2[\text{Cu(NCS)}_2]\). The \(ET\) crystal was attached to a thermometer which was suspended by 0.0025 cm diameter gold electrical leads. When exposed to room temperature radiation, the detector reached an operating temperature of 6.5 K. Thermal conductance of the leads is estimated from the load curve measurement while the absorbed power is approximated using this value combined with the 2 K temperature difference between the \(^4\text{He}\) cold stage and the bolometer temperature. Also included in the table is the measured current noise which, unfortunately, dominates all the other sources completely.

### 2.1.3 Experimental Details

Schematic diagrams of the mounting configuration used in these measurements are shown in Figures 2.4 and 2.5. The sample mount, made of oxygen-free-high-conductivity
Table 2.2: The various noise contributions have been estimated for one of the ET crystal composite bolometers used in these experiments.

<table>
<thead>
<tr>
<th>Noise Term</th>
<th>Relevant Parameters</th>
<th>Noise Contribution $W^2/Hz$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2k_B T_B \varepsilon P_B$</td>
<td>$T_B = 300K, \varepsilon P_B = 50\mu W$</td>
<td>$4.2 \times 10^{-25}$</td>
</tr>
<tr>
<td>$4k_B T^2 G$</td>
<td>$T = 6.5K, G = 23 \frac{mW}{K}$</td>
<td>$0.54 \times 10^{-25}$</td>
</tr>
<tr>
<td>$4k_B T^2 S^2 \left(\frac{R}{R_L+R}\right)^2$</td>
<td>$T = 6.5K, R = 1.4 M\Omega, S = 3 \times 10^4 \frac{V}{W}$</td>
<td>$5.6 \times 10^{-25}$</td>
</tr>
<tr>
<td>$\frac{N^2}{\omega S^2}$</td>
<td>measured, $I = 0.8\mu A, f = \frac{\omega}{2\pi} = 5Hz$</td>
<td>$2 \times 10^{-24}$</td>
</tr>
</tbody>
</table>

(OFHC) copper, has a wedged light guide to help reflect extra light onto the sample surface. Reflections from the polished flat faces of the light guide preserve the polarization with $\vec{E}$ parallel to the face, but introduce a perpendicular component to the other polarization. Mounts were made out of two pieces to allow polishing of the inside reflecting surfaces. After these surfaces were polished, the two pieces were held together using screws and the entire mount was electroplated with gold to prevent tarnishing. In the cryostat, the sample mount was held in place using stainless steel screws and was thermally isolated from the 4.2 K cold stage using stainless steel washers. Sample temperature could then be adjusted by either varying the thermometer bias current or by controlling the current through an external heater. Using the external heater allowed setting of the bolometer current to maximize the sensitivity and minimize current noise. Microwave absorbing material absorbed any radiation that would pass by the sample.

Figures 2.6 and 2.7 are photographs showing details of one of the samples mounted for bolometric measurements. The sample, with a bolometer thermometer glued to the back, was suspended in the middle of the 1.5 mm gap at the bottom of the light guide wedge. Mounted next to the sample is a small mirror which allowed reflectivity measurements.
Figure 2.4: Sectional view of the sample mount for bolometric measurements. Stainless steel shims provide some thermal isolation between the sample mount and the \(^4\)He cold stage, allowing temperature control using an external heater mounted on the side.
Figure 2.5: A perspective view of the bolometric sample mount. As viewed from the front, the thermometer is completely hidden behind the sample.
Figure 2.6: Photographs of the sample mount used for bolometric absorption measurements.
Figure 2.7: Close-up photographs of a composite bolometer made using a single crystal \((BEDT-TTF)_2[Cu(NCS)_2]\) sample and a doped silicon thermometer.
to also be performed on this sample. The upper close-up photograph in Figure 2.7 shows two reflected images of the sample in the sides of the light guide. From this photograph, it is seen that the thermometer is completely hidden behind the sample.

Making such a composite bolometer is a delicate procedure, and was accomplished working almost entirely under a microscope. First, the solder pads for the thermometer leads were glued in place, about 0.5 cm apart on either side of the gap, using Miller-Stephenson epoxy for both bonding and electrical insulation[95]. Indium alloy solder was then used to attach the constantan alloy wires, which led from these pads to the connecting pins on the outside of the mounting block. After the constantan wires were held in place with epoxy, the solder was melted again to bond the 0.0025 cm diameter gold electrical leads for the thermometer. With a working platform at the appropriate height, the gold wires were then bent into position to reach the electrical contacts on the bolometer thermometer, and the thermometer was slid into place. A fine filament of glass, made by melting and stretching a 2 mm diameter rod, was then used to apply a small amount of conducting epoxy to hold the wires in place. When this glue was set, the sample mount was raised above the working platform, the sample set in place, and a small amount of glue applied to the surface of the thermometer (non-conducting, Miller–Stephenson epoxy) before lowering the thermometer back down onto the sample. The sample mount was clamped in position for the 24 hours it takes for the glue to set at room temperature.

The sample was positioned at the focus of a Beckmann FS-720 polarizing far-infrared Fourier transform spectrometer. By varying the size of the source aperture, it was possible to either focus all of the spectrometer radiation onto the sample surface or obtain extra intensity from the light reflected from the light guide walls.

A time constant of less than 100 msec was desired for the bolometers used in these experiments. For the single crystal organic superconductors, with typical dimensions
0.1 \times 0.2 \times 0.01 \text{ cm}^3, \text{ the 0.0025 cm gold thermometer leads provided appropriate thermal contact. For other experiments, using both a sapphire calibrating absorber and high-}\text{ }T_c\text{ superconductors, additional thermal links were used as necessary. Spectrometer radiation was chopped at a rate of approximately 5 Hz and the bolometer voltage was amplified with a room temperature pre-amplifier before going to a lock-in amplifier and integrator.}

2.1.4 Thermometry and Maximization of Signal/Noise

Two cooling runs were usually performed to characterize the bolometer before attaching the organic crystal for sample absorption measurements. One cooling was used to calibrate the thermometer resistance as a function of temperature and the other was used to measure a load curve and noise characteristics of the thermometer in the bolometric configuration.

A glass $^{4}\text{He}$ dewar was used for bolometer thermometer calibration. The sample and a reference thermometer were contained in a double walled copper can which could be moved vertically above the liquid. A vacuum space between the inner and outer walls of the calibration can prevented the temperature gradient in the $^{4}\text{He}$ gas in the cryostat from being seen inside the can. Atmospheric pressure gas kept the temperature uniform within the calibration volume and ensured equal temperatures for the sample and a reference thermometer. Above 4.2 K, the temperature could be set by adjusting the height of the can above the liquid. For temperatures at and below 4.2 K, the can was submerged in the $^{4}\text{He}$ and the temperature was lowered by pumping on the $^{4}\text{He}$ vapour.

A carbon resistor, with smoothly varying temperature dependence between room temperature and $^{4}\text{He}$ temperatures, was used as the reference thermometer. A logarithmic function was fit to pass through the room temperature, 77 K liquid nitrogen, and pumped $^{4}\text{He}$ calibration points. Pressure measured using a Diavac pressure gauge (calibrated using both oil and mercury manometers) was used in combination with the published $^{4}\text{He}$
vapour pressure curves to determine temperatures below 4.2 K[96, 91]. The calibration is reliable to within ±0.01 K around 4.2 K or ±0.1 K for temperatures approaching 15 K.

The bolometer thermometers, which came from Harvey Moseley at NASA, are boron-doped silicon. Experiments for which these thermometers were intended are conducted exclusively below 1 K, but mistakes in the manufacturing procedure resulted in several batches of incorrectly doped thermometers, more suitable for use in the temperature range above 4 K. Thermometer dimensions are about $0.03 \times 0.03 \times 0.05 \text{ cm}^3$, with one of the larger surfaces having two aluminum pads for bonding thermometer leads. Aluminum was used for these pads to allow bonding of aluminum wires which would be in the superconducting state at the intended operating temperature. Unfortunately, it was found that simply connecting gold wires to the aluminum pads using conductive paint or epoxy resulted in severe current noise problems, most likely caused by an insulating aluminum oxidation layer. Much better noise characteristics were obtained by ultrasonically bonding gold balls onto the pads and attaching the wires to the clean gold surface.

In order to measure optical absorption spectra above and below the 10.4 K superconducting transition temperature of $(\text{BEDT-TTF})_2[\text{Cu(NCS)}_2]$, it was necessary to choose a thermometer which compromised between high sensitivity and wide operating range. NASA thermometers from two different batches were useful for our experiments. Resistance as a function of temperature for these two groups of thermometers are shown in Figure 2.8 along with data for a similar commercial detector thermometer specifically designed for use at $^4\text{He}$ temperature. The commercial thermometer clearly has the highest thermal coefficient of resistance at low temperature, but the resistance drops too quickly to allow use above 8 K[94]. Both groups of NASA thermometers have a relatively low coefficient of resistance but will give reasonable sensitivity over a broader temperature range.

A load curve measured for one of the NASA thermometers is shown in Figure 2.9 and
Figure 2.8: Two thermometers from Harvey Moseley at NASA have nearly parallel resistance as a function of temperature. A third thermometer, commercially made and designed for use at 4.2 K, shows a much higher coefficient of resistance at low temperature, but has very low sensitivity at 10 K.
Figure 2.9: Load curve measured for one of the NASA thermometers at a temperature of 8.5 K.
the derived sensitivity as a function of bias current is shown in Figure 2.10. Superimposed on the plot of the calculated sensitivity is the actual absorption signal, measured over the same range of bias currents. Absorption signal and calculated sensitivity have a roughly similar shape but agreement is not exact. The problem is that there is some current dependence to the bolometer resistance which distorts the load curve, especially at low currents[97]. For this reason, the calculated sensitivity from the load curve gives only a very rough estimate of the actual bolometric sensitivity, and the optimum detector current is best chosen by maximizing the measured signal to noise ratio for absorbed radiation.

Thermometer noise was measured using the circuit shown in Figure 2.11. A Princeton Applied Research (PAR) 113 preamp was used to both amplify the signal and set the desired bandpass for the noise spectrum. Root–mean–square (rms) voltage was measured using the ac voltmeter function of the PAR 124 lock–in amplifier. Noise amplitude measured as a function of frequency is shown in Figure 2.12 and displays both amplitude proportional to current and $1/f$ frequency dependence typical of current noise.

Load curve and noise measurements for one of the NASA thermometers and the commercial thermometer element are compared in Table 2.3. It is clear that the commercial thermometer has much lower sensitivity at high temperatures. A secondary effect of the commercial thermometer’s low resistance at 10.5 K is that maximization of sensitivity requires higher measuring current. Thus, not only is the sensitivity low, but there is also a much greater problem with current noise. This is especially evident in the large uncertainty in the rms noise voltage which was associated with a large shot noise contribution. The measured NEP shown in the table is a practical value derived from the signal to noise ratio measured for absorption of radiation using the formula:

$$NEP = \frac{Signal\ Voltage}{Sensitivity} \times \left( \frac{Signal}{Noise} \right)$$  \hspace{1cm} (2.6)
Figure 2.10: Bolometer sensitivity is derived from the load curve and shows a maximum in agreement with the measured maximum signal for absorbed radiation.
Figure 2.11: The circuit for measuring thermometer noise used a PAR 113 preamp to set the bandpass and a PAR 124 lock-in amplifier in the ac voltmeter mode to measure the rms noise voltage.
Figure 2.12: A measurement of bolometer noise as a function of frequency shows $1/f$ dependence. This, along with the increasing amplitude with higher current indicates that the dominant contribution is the current noise term in Equation 2.5.
Table 2.3: Bolometer sensitivity at two operating points.

<table>
<thead>
<tr>
<th></th>
<th>Moseley, Batch 11-4 T=5.3 K</th>
<th>Moseley, Batch 11-4 T=10.5 K</th>
<th>I. R. Labs 4.2 K Thermometer T=10.5 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{bol}(M\Omega)$</td>
<td>0.80</td>
<td>0.12</td>
<td>0.009</td>
</tr>
<tr>
<td>Optimum Bias Current (max. Sig/Noise) ($\mu A$)</td>
<td>1.5</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>Load Curve Sensitivity ($V/W$)</td>
<td>$-6.0 \times 10^4$</td>
<td>$-4.5 \times 10^3$</td>
<td>$-6.0 \times 10^2$</td>
</tr>
<tr>
<td>(0.1–10 Hz) Noise (rms) Voltage ($\times 10^{-9} V/\sqrt{Hz}$)</td>
<td>80 ± 10</td>
<td></td>
<td>130 ± 80 (large uncertainty due to shot noise)</td>
</tr>
<tr>
<td>Measured NEP ($W$) (with 5 Hz signal, 16 sec integration)</td>
<td>$0.7 \times 10^{-12}$</td>
<td>$5.3 \times 10^{-12}$</td>
<td>$800 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

where the ratio of signal/noise was measured on a chart recorder after signal integration with a 16 sec time constant.

2.2 $TTF-TCNQ$ Bolometric Absorption Spectrum

Before attempting measurements on the organic superconductors, several tests of the experimental technique were undertaken. The first was to construct a composite bolometer using the organic conductor, $TTF-TCNQ$, which is a material with well studied spectral absorption characteristics. Absorption measurements using this sample are a little bit easier than those on the organic superconductors because $TTF-TCNQ$ undergoes a Peierls transition at 60 K. At low temperatures where the bolometric measurements are carried out, the sample is semiconducting and the far-infrared reflectivity has a relatively low level of between 85% and 95%[98, 99]. This low reflectivity results in an absorption signal which is relatively strong.
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The absorption spectrum measured using the TTF – TCNQ composite bolometer, and divided by an instrumental background, is shown in Figure 2.13(a). This can be compared with a published spectrum in 2.13(b), which was measured using the sample itself as a thermometer in a direct bolometric technique[100]. Although the new spectrum was measured with lower resolution, similar features are clearly present. All of the strong absorption features, which were previously assigned to specific phonon vibrations of the TTF and TCNQ molecules, are accurately reproduced.

The success of this measurement indicated that it would be feasible to undertake bolometric studies of the organic superconductors, even considering the fact that the signal might be approximately 10 times smaller for the samples which are metallic rather than semiconducting at low temperatures.

2.3 Background Spectra from a Golay Detector and a Composite Bolometer

For measurements on organic superconductors, it is important to know not only the frequencies of the spectral features but also the wavenumber dependence of the absorptance. This requires an accurate determination of the instrumental background spectrum. Most of our background spectra were measured using a Golay detector, one of the few detectors known for having a frequency-independent response over a wide spectral range. However, in order to confirm that the Golay detector and a bolometric absorber actually observe the same incident spectrum, a composite bolometric detector was constructed using a sapphire–metal film absorber. This type of absorber was chosen because the optical response can be calculated and compared with the measured response. The bolometrically measured spectrum, divided by the background measured using the Golay detector, should have wavenumber dependence in agreement with the calculated absorption spectrum. The level of agreement between the experimental result and the calculation will
Figure 2.13: (a) An absorption spectrum measured for the organic conductor TTF–TCNQ using the composite bolometric technique shows sharp absorption features corresponding to TTF and TCNQ molecular phonon frequencies. (b) Previous published absorption spectrum of TTF–TCNQ, measured using the direct bolometric technique[100].
give an indication of the wavenumber–dependent accuracy of the bolometric measurements.

2.3.1 Golay Detector

In the far-infrared, the signal from a Golay detector is almost completely independent of the frequency of the incident light. Within the Golay detector is a very thin metallic film which absorbs most of the incident radiation. The absorption takes place through the response of the conduction electrons and thus does not vary from the dc response until the plasma frequency for the metal is reached, usually near the optical region. With absorption governed by the nearly free electron behaviour, the Golay detector has a flat response over a wide range of frequencies, from the far-infrared up to nearly the visible.

The way in which the Golay cell converts the absorption at the metal film to an electrical signal is shown in Figure 2.14. Power absorbed produces a temperature change in the gas contained in a closed volume. One wall of this gas chamber is a flexible metallized membrane which distorts when the gas temperature (and pressure) changes. This flexible surface is used as a mirror in a separate optical source and detector system which is arranged to be very sensitive to mirror distortions, and provides an output signal from the detector.

The only factor which distorts the flat frequency response of a Golay detector is absorption by the diamond window to the pneumatic cell. Diamond is one of the best choices for a window in the far-infrared, having flat transmission characteristics over a very wide range. In the far-infrared region, the only deviation is a phonon feature in the region around 500 $cm^{-1}$, which lowers the signal by about 10% in a narrow frequency range.
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2.3.2 Sapphire–Thin Film Absorption

A bolometer made using a sapphire–metal film as an absorber has optical characteristics which can be predicted based on the published optical properties of sapphire and the impedance of the conducting film. Because the sapphire is in the form of a thin wafer, the calculations must include detailed analysis of multiple internal reflections, and the resulting absorption modulations known as channelling in the spectrum. For a certain choice of the metal film impedance, these internal reflections can be eliminated to give the absorber a flat, frequency independent response.

Absorption Calculation

One relatively simple way to calculate the optical response of a sapphire–metal film bolometer is using equations analogous to those used in a standard treatment of transmission lines[102, 103]. By considering the impedance mismatch at a boundary between two regions of dielectric, it is possible to derive the transmitted, absorbed, and reflected
portions of the incident light. In the calculations outlined here, only the case of normal incidence on a plane interface will be considered, although it is possible to do a similar calculation in the more general case of non-normal incidence.

It is useful to start by looking at the situation where there are three different regions, as shown in Figure 2.15. For normally incident light with wavenumber, $\bar{v}$, the load impedance seen at the first interface is:

$$Z_{L1} = \eta_2 \left[ \frac{\eta_3 \cosh \gamma_2 d + \eta_2 \sinh \gamma_2 d}{\eta_2 \cosh \gamma_2 d + \eta_3 \sinh \gamma_2 d} \right], \quad (2.7)$$

where the impedances, $\eta$, and propagation coefficients, $\gamma$, for the different regions are given by:

$$\eta = \sqrt{\frac{\mu_0}{\varepsilon_0 \varepsilon}} = \frac{377 \Omega}{n + i\alpha/4\pi \bar{v}}$$

$$\gamma = i\omega\sqrt{\mu_0 \varepsilon_0 \varepsilon} = \frac{\alpha}{2} + 2\pi i n \bar{v}. \quad (2.8)$$

Here, the absorption coefficient, $\alpha$, and the wavenumber, $\bar{v}$, are both in cm$^{-1}$ and $1/\sqrt{\varepsilon_0 \mu_0} = c = 3 \times 10^8$ m/sec and $\sqrt{\mu_0 / \varepsilon_0} = 377 \ \Omega$. The reflectance coefficient and the total power reflected are:

$$R = \frac{Z_{L1} - \eta_1}{Z_{L1} + \eta_1}$$

and the transmission is:

$$T = \frac{2Z_{L1}}{Z_{L1} + \eta_1}.$$

In a case where the absorption coefficient is negligible, the impedance, $\eta$, is directly proportional to $1/n$, and it is evident that these equations for $R$ and $T$ reduce to the
Incident

Reflected

Transmitted

\( \eta_1 \)

\( \eta_2 \)

\( \eta_3 \)

\( d \)

\[ Z_{L1} = \eta_2 \left[ \frac{Z_{L2} \cosh \gamma_2 d + \eta_2 \sinh \gamma_2 d}{\eta_2 \cosh \gamma_2 d + Z_{L2} \sinh \gamma_2 d} \right]. \]  

(2.11)

For the sapphire–metal film bolometer, the load impedance at the back of the sapphire is a thin metal film as shown in Figure 2.16. The important characteristic of the metal film is that the real part of the conductivity, and thus the imaginary part of \( \varepsilon \), is large. Considering the case of the film (with impedance, \( \eta_m \)) in air and in the \( d \to 0 \) limit,
Equation 2.7 becomes:

\[ Z_L = \frac{\eta_0 + (\eta_m \gamma_m)d}{1 + \eta_0(\gamma_m/\eta_m)d}. \]

(2.12)

The term, \((\eta_m \gamma_m)d\), in the numerator is negligible for small \(d\) because the factors of \(e^{-1/2}\) and \(e^{1/2}\) from \(\eta\) and \(\gamma\) cancel out. In the denominator however, the term proportional to \(d\) must not be neglected because the factor \((\gamma_m/\eta_m)\) is proportional to \(\epsilon\) (and the real part of the conductivity, \(\sigma_r\)). In the limit where \(d\) is small, the equation for the load impedance of a thin metallic film becomes:

\[ Z_L = \frac{\eta_0}{1 + \eta_0d(\gamma_m/\eta_m)} = \frac{\eta_0}{1 + \eta_0d(i\omega\epsilon)} \approx \frac{\eta_0}{1 + \eta_0/\sigma_r} \]

(2.13)

Here, \(R_\square = 1/\sigma_r d\), is the dc resistance which would be measured for a square section of the metal film.

From Equation 2.11, it is clear that channelled spectra modulations will be eliminated if \(Z_L\) is equal to \(\eta_2\). Sapphire has \(\alpha \approx 0\) and \(n \approx 3\) in the far-infrared region so the metal film impedance should be chosen to give \(Z_L = \eta_0/3\). In this case, Equation 2.13 shows that the required film impedance is \(R_\square = \frac{1}{2}\eta_0 = 188\,\Omega/\square\).

Calculations of the absorptance of a sapphire--metal film system were performed for several choices of \(R_\square\) and are shown in Figure 2.17. Frequency dependence of the optical constant of sapphire, as taken from published low temperature measurements, makes it impossible to get a perfect impedance match over a wide spectral range[104]. Over the region from \(40\,\text{cm}^{-1}\) to \(300\,\text{cm}^{-1}\), the optical constant changes quite significantly, going from \(n(40\,\text{cm}^{-1}) = 3.052\) up to \(n(300\,\text{cm}^{-1}) = 3.636\). From the three curves shown in Figure 2.17, it is seen that \(R_\square = 175\Omega\) gives the flattest response, with \(A=50\%\), \(R=25\%\), and \(T=25\%\).

One interesting and important feature of these calculations is that the phase of the modulations changes when the substrate--film impedance mismatch changes sign. To
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Figure 2.16: Bolometer substrates are often made using a sapphire–metal film absorber as shown here. When the load impedance, $Z_L$, is chosen to match the impedance of the sapphire, $\eta_s$, internal reflections and channelling in the absorption spectrum are eliminated.

\[ Z_L = \frac{\eta_0}{1 + \eta_0/R_s} \]
Figure 2.17: A metal film with $R_\square \approx 175\Omega/\square$ gives the sapphire-metal film almost frequency independent response in the far-infrared. When the resistance has any other value, channelled spectra will be observed with phase depending on whether the impedance is higher or lower than $175\Omega/\square$. 
analyse such a mismatched film, it is useful to complete the algebra to derive the absorptance explicitly. In the simplified case where the sapphire absorption coefficient is neglected, the result is\[105\]:

\[
A = \frac{T_1(1 - T_2 - R_2)}{1 + R_1 R_2 \pm 2(R_1 R_2)^{1/2} \cos \delta}
\] (2.14)

where:

\[
R_1 = \frac{(n - 1)^2}{(n + 1)^2} \quad T_1 = \frac{4n}{(n + 1)^2}
\] (2.15)

\[
R_2 = \frac{(1 - n + \eta_0/R_\square)^2}{(1 + n + \eta_0/R_\square)^2} \quad T_2 = \frac{4n}{(n + 1 + \eta_0/R_\square)^2}
\] (2.16)

\[
\delta = 4\pi nd\bar{\nu}.
\] (2.17)

Choice of sign in the denominator of Equation 2.14, accounts for the change in phase on reflection depending on the impedance mismatch. The plus sign is used if $Z_0/R_\square > n - 1$, while the minus sign applies if $Z_0/R_\square < n - 1$. Once again, for sapphire with $n_{\text{sapp}} \approx 3$, the channelled spectra are eliminated by choosing $R_\square = \frac{1}{2}\eta_0$, which results in $R_2=0$.

**Measured Sapphire Bolometer Absorptance**

To make an absorber suitable for checking the accuracy of the bolometric measurements, a piece of sapphire was cut to have an absorbing surface with a size similar to the organic samples. Dimensions were $0.1\ cm \times 0.7\ cm \times 0.01\ cm$ and a bismuth metal film was evaporated onto the back surface. During evaporation, resistance of a film deposited on a surface near the sapphire absorber was monitored and evaporation was stopped when the desired impedance was reached.

A composite bolometer was made by suspending the sapphire–metal film absorber in a mount similar to that used for organic crystal bolometric measurements. The size of the absorber made it necessary to shorten the time constant by using $0.0025\ cm$ gold wires to support the substrate. Because the piece of sapphire used here was long and narrow,
it was possible to glue the bolometer thermometer to one end where it was completely shielded from incident radiation.

A measured spectrum for the sapphire–metal film bolometer, shown in Figure 2.18, clearly demonstrates that the desired impedance match at the back surface was not obtained. After dividing the sapphire bolometer absorptance by a Golay background signal, a channelled spectrum is measured throughout the far-infrared region. Despite this undesirable film impedance mismatch, the bolometric absorption spectrum was still useful because detailed analysis allowed estimation of both the thickness of the sapphire and the impedance of the metal film. Calculations for the absorptance of a mismatched sapphire–metal film system were then carried out, and the result was compared to the measured spectrum.

According to Equation 2.14, peaks due to multiple internal reflections occur each time $4n_{\text{sapp}}d\bar{\nu}$ is either an even or odd integer, depending on the sign used in the denominator. For $Z_0/R_\square > n - 1$, the sign is positive and peaks should correspond to values of $4\pi nd\bar{\nu} = \text{odd integer} \times \pi$, while for $Z_0/R_\square < n - 1$, peaks occur when $4\pi nd\bar{\nu} = \text{even integer} \times \pi$. For peaks corresponding to even integers, there is a maximum at $\bar{\nu} = 0$, while for odd integers, the first peak occurs when $4n_{\text{sapp}}d\bar{\nu} = \pi$ and there is a minimum at $\bar{\nu} = 0$.

Using the data in Figure 2.18, even integers were assigned to the peaks and plotted as a function of $4n_{\text{sapp}}\bar{\nu}$. The result is a straight line with the intercept at the origin as shown in Figure 2.19. The slope of the straight line through the data gives the film thickness, $d = 0.0105 \text{ cm}$, and the good fit confirms the variation of the sapphire optical constant in this frequency range. The position of the intercept at the origin indicates that the assignment of even integers ($R_\square$ too large) to the peak positions was correct. Assignment of odd integers would displace the points in Figure 2.19, and the intercept on the $y$ axis would move up to the integer value of $+1$. This would imply a peak at $\bar{\nu} = 0$, rather than the required minimum. Thus, it is concluded that $\eta_0/R_\square < n - 1$, indicating
Figure 2.18: Channelling in the sapphire–metal film absorptance demonstrates a poorly matched impedance for the evaporated metal film. Modulations become more closely spaced at higher frequencies as the sapphire index of refraction increases.
that the deposited film was thinner than would be required for the perfect impedance match.

Knowing that the resistance of the film is too high, the value of $R_0$ which would give the observed ratio of overall absorptance to modulation amplitude can be estimated. The sapphire–metal film bolometric absorption signal, divided by the Golay background, is again shown in Figure 2.20, with the calculated bolometer absorptance obtained using $R_0 = 300 \pm 50\Omega$ superimposed.

The fact that there is a good fit between the bolometer absorptance and the theoretical calculation shows that the Golay detector measures a spectrum proportional to the light intensity incident on the small bolometric absorber. Beneath the interference fringes, both the measured and calculated spectra are flat in the region from 50 $cm^{-1}$ to 350 $cm^{-1}$. An uncertainty level in the wavenumber dependent accuracy of the absorptance is estimated to be ±10%, and becomes quite negligible for highly reflecting samples, especially after the signal is converted from absorptance to reflectivity.

From these experiments, it was also determined that it is important that the same spectral beam be incident on both the sample and the reference detector. For this to be the case, both sample and reference detector must be positioned at an instrumental focus, and the light must be entirely focused onto the sample surface. In the original instrumental configuration, the instrument focus was at the centre of the sample chamber and the Golay detector was positioned well behind this point (similar to position M6 in Figure 1.29). The first problem with this configuration is that the signal is low because the detector does not collect all of the spectrometer beam. The second problem is that the spectrum is distorted because the off-axis parts of the beam do not reach the detector. This means that most of the light getting to the detector has travelled almost exclusively along the central beam axis where the alignment of the instrument is the best. Moving the detector to the position of the focus not only increases the overall signal, but also
Figure 2.19: Assigning an even integer to each of the channelled spectrum peaks and plotting as a function of $4n_{\text{sapp}}\nu_{\text{peak}}$ gives a straight line with slope, $d = 0.0105\,\text{cm}$ and intercept at the origin. The intercept at the origin indicates that the channelling of the spectra results from a value of $R_\sigma$ which is higher than the desired value.
Figure 2.20: The best fit for the data is obtained with a sapphire substrate of thickness, $d = 0.0105 \text{ cm}$, and film resistance, $R_0 = 300\Omega$. 

Sapphire-Metal Film Absorptance

- --- Sapphire-metal film calculation. $R_0 = 300\Omega$, $d = 0.0105\text{ cm}$
- --- Measured absorptance divided by Golay background
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results in a spectrum which includes some poorly modulated, high frequency signal.

2.4 Bolometric Absorption of the High-\( T_c \) Superconductor, \( YBa_2Cu_3O_7 \)

Bolometric absorption measurements on this high-\( T_c \) superconductor were undertaken to look for a superconducting gap. At the time these experiments were conducted, there was some controversy over reflectivity measurements which were being scaled to give 100% reflectivity at low frequency. Absorption measurements have an advantage over the reflectivity measurements because 100% reflectivity implies absolutely zero absorptance. Any drop from finite absorptance to absolutely zero should be easily observed, especially because the spectral region of the gap for high-\( T_c \) materials is at a relatively high frequency. With a superconducting transition temperature at 90 K, the contribution to absorptance from conventionally paired BCS electrons should drop to zero at a frequency of about \( 220 \ cm^{-1} \). Using the readily available high-\( T_c \) samples in the form of pellets and thin films, and working in this relatively high frequency range, it is not difficult to obtain a low temperature absorptance signal bolometrically.

\( YBa_2Cu_3O_7 \) Sample Preparation

The sample used in these experiments was made by Paul Schleger at U.B.C. Pellets were made by taking many very small crystals of the high-\( T_c \) material, and pressing them into disks 1 cm in diameter and about 40 \( \mu m \) to 80 \( \mu m \) thick. After the pressing, the samples were sintered at high temperature to encourage amalgamation of the small starting crystals. Because the starting crystals are thin platelets, with the poorly conducting \( c \)-axis perpendicular to the flat surface, the pressed pellets also end up with the \( c \)-axis largely perpendicular to the surface. By looking at the x-ray diffraction signal while rocking the sample, it was estimated the angular variation in the \( c \)-axis orientation at the surface
was ±3 degrees. Oxygen content was carefully controlled and superconducting properties were established using other techniques, including dc resistivity.

A small piece, roughly 0.45 cm $\times$ 0.4 cm, of one of the pressed pellets was used as the absorber for a composite bolometer. It was supported by a total of six 0.0025 cm gold wires at the end of a 19° light cone, and was big enough to almost entirely fill the 4 mm circular cone exit. The light cone angle and exit size were chosen to focus light from a 12 mm diameter area onto the sample, giving an acceptance area similar to the golay detector used for the background measurements.

A doped silicon thermometer, with $R(4.2 \text{ K})=7 \, \text{M} \Omega$, was glued to the back of the sample. Because the piece of high-$T_c$ superconductor was relatively large, the thermometer was well shielded from any radiation that might leak by the edges. With pumped $^4\text{He}$ in the cryostat and no cold filters in front of the absorber, the thermometer resistance was 420 $\text{K} \Omega$, corresponding to a temperature below 10 K, and the time constant for response to radiation was between 5 msec and 10 msec. Bias current through the thermometer during the measurements was 20 $\mu A$ and the signal was amplified and then measured using the PAR 124 lock-in amplifier.

$YBa_2Cu_3O_7$ Absorption Results

The absorption spectrum for this $T_c=90 \, K$ superconductor, measured at a temperature below 10 K, is shown in Figure 2.21. There are many strong phonon features in this far-infrared region and, although the absorptance is dropping rapidly at lower frequencies, there is clearly continued absorption below the BCS energy gap, $2\Delta \approx 220 \, \text{cm}^{-1}$. These results are in good agreement with the data obtained in reflectivity measurements on similarly prepared sintered samples[106]. More recent work with single crystals has demonstrated that most of the strong phonon absorptions are due to absorption of the light polarized along the poorly conducting $c$-axis rather than the highly conducting $a$-$b$
Similar measurements were performed on a BiSrCaCuO thin film deposited on an MgO substrate. Once again, the highly conducting crystalline plane was parallel to the sample surface. No evidence of a superconducting gap was observable in the optical absorption spectrum.

Non-zero absorptance, for the high-$T_c$ superconductors in the far-infrared at temperatures below $T_c$, has now been observed in many cases. It is thought that this absorption is taking place through mechanisms other than interactions with the conduction electrons. In order to associate spectral features in an absorption measurement with the superconducting transition, it is necessary to compare measurements with the sample in the superconducting and normal states. Using the bolometric technique with doped silicon thermometers, measurements at temperatures above the superconducting transition are impossible. Another option is to establish the normal state by application of a magnetic field. However, this could only be achieved using a cryostat specifically designed to hold superconducting magnets since, for the high-$T_c$ thin film superconductors in particular, a very high applied field is required.

### 2.5 BEDT-TTF Results

With the lower superconducting transitions of the organic superconductors, a single doped silicon thermometer can be used to obtain bolometric absorption measurements at temperatures above and below $T_c$. Optical measurements are much more difficult than with the high-$T_c$ samples however, because the organic superconducting samples are always very small and fragile. These characteristics make the focusing of light onto the sample difficult and the sample itself is susceptible to damage through handling and
Figure 2.21: Bolometric absorption measurements of the high-$T_c$ superconductor, $YBa_2Cu_3O_7$ display strong phonon features and absorption all the way down to the lowest frequencies. This is in agreement with measurements on similar samples using reflectivity techniques[106].
thermal cycling. The major disadvantage of the lower superconducting transition temperature is that the energy region affected by the superconducting transition lies in the far-infrared, where the source intensity is much weaker.

2.5.1 Bolometric Absorption of \((BEDT-TTF)_2AuI_2\), with \(T_c = 3.8\) K, Above and Below \(T_c\)

One of the first ET based superconductors to have an ambient pressure superconducting transition at a relatively high temperature is \((BEDT-TTF)_2AuI_2\). In these crystals, the ET molecules are arranged in stacks, giving some anisotropy to the electrical and optical properties. Bolometric absorption measurements using one of these crystals were performed at temperatures above and below the superconducting transition at 3.8 K.

Sample Analysis and Preparation

Crystals of \((BEDT-TTF)_2AuI_2\) were grown at U.B.C. by Frances Bates using an electrochemical technique. By carefully controlling conditions, such as the temperature and the current through the electrolytic cell, it was possible to obtain crystals in the form of thin platelets with a reasonably large size. The largest crystals, which were used for the bolometric absorption measurements, had absorbing areas of about 0.1 \(cm \times 0.2\) \(cm\).

Like many of the ET based materials, \((BEDT-TTF)_2AuI_2\) has several non-superconducting phases in addition to the superconducting phase with \(T_c = 3.8\) K. The different phases can be distinguished at room temperature using electron-spin-resonance measurements. Peak to peak separation in the ESR spectrum is 18 G to 20 G for the crystal of the superconducting \(\beta\)-phase, while the other two possible phases have separations of 10 G to 15 G and 27 G to 35 G[79]. ESR peak separation for the crystals used in these experiments was about 19 G, confirming the superconducting phase of the material.
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Orientation of the crystalline axes was determined using room temperature mid-infrared reflectivity measurements. In the region between 500 cm\(^{-1}\) and 3000 cm\(^{-1}\), the room temperature reflectivity for light polarized along the highly conducting stacks is much higher than that for light polarized perpendicular to the stacks[57]. Measured reflectance spectra for these polarizations were similar to the published results, but the absolute magnitude was about 10% lower because sample and mirror orientations were only roughly aligned.

After the orientation of crystalline axes was determined from the room temperature reflectivity, the crystal was glued to one of the thermometers to make a composite bolometer. A bolometric mount similar to that shown in Figure 2.5 was used and the crystal orientation was chosen so that the light polarized with \(\vec{E}\) parallel to the stacks would be preserved in reflections from the flat sides of the light guide. Thermal conduction between the absorbing sample and the mount was through the thermometer 0.0025 cm diameter electrical leads.

Absorption measurements were made with sample temperatures both above and below the superconducting transition. With no cold filters in front of the sample, measurements were made in the region from 20 cm\(^{-1}\) to 400 cm\(^{-1}\) at the minimum bolometer temperature of 5.7 K. Although cold filters allow lower temperature measurements, they also limit the spectral range and make it difficult to obtain accurate background spectra, since any useful background measurement requires that the filters be present and cooled to the same low temperature. Sample absorption measurements, looking for an effect of the superconducting transition, were performed with cold filters removing all background radiation above the frequency of 50 cm\(^{-1}\). Using this configuration, sample temperatures below \(T_c\) were obtained and spectra were measured covering the region from about 5 cm\(^{-1}\) up to 50 cm\(^{-1}\) at temperatures of 3 K and 4.4 K.
Chapter 2. Bolometric Measurements

\((BEDT-TTF)_2AuI_2\) Absorption Results

Measurements of absorbed signal as a function of chopping frequency indicated that some of the incident radiation was absorbed directly by the thermometer rather than the sample. At high chopping rates, the signal was due to direct radiation heating the thermometer by itself and leaving the relatively large \((BEDT-TTF)_2AuI_2\) crystal at constant temperature. As the chopping frequency was lowered, the signal increased dramatically as the radiation absorbed by the sample began to affect the thermometer. Several tests had to be performed in order to ensure that this leakage radiation was not larger than the sample absorption.

Direct thermometer absorption has specific spectral features which lead to large differences in the spectra measured at low and high chopping frequencies. With the chopping frequency at 80 Hz, the measured signal had a large peak at 360 \(cm^{-1}\), which is characteristic of direct thermometer absorption as shown in Figure 2.22. At a chopping frequency of 5 Hz, the 360 \(cm^{-1}\) thermometer absorption peak no longer dominates the spectrum, since most of the heating takes place through absorption by the sample. Comparison of these spectra indicates that with low chopping frequency, most of the signal is due to sample absorption.

Further evidence that direct thermometer absorption does not overwhelm sample absorptance at low chopping frequency is seen in the polarization dependence of the signal amplitude. For high chopping frequencies, there was a ratio of 3:1 between vertically and horizontally polarized light. This is due to the direct thermometer absorption being polarization independent, giving the ratio expected for the instrumental polarization. For low chopping frequencies, the polarization dependence of the sample absorption caused the signal amplitude to deviate from the 3:1 instrumental ratio. Because the highly absorbing sample axis was aligned with the weak instrumental polarization, the ratio of
Figure 2.22: Direct thermometer absorption shows a strong peak at 360 cm$^{-1}$, and relatively low absorption at lower frequencies.
maximum to minimum absorption signals was reduced to 1.6:1.

Absorption spectra were first obtained without cold filters to allow measurements covering a wide spectral range. In the 100 $cm^{-1}$ to 370 $cm^{-1}$ range, shown in Figure 2.23, spectra were measured with 4 $cm^{-1}$ resolution and light was allowed to reflect from the light guide walls onto the sample. Figure 2.23 shows absolutely no peaks or phonons which could be associated with molecular vibrations, and there is only a slight rise at 350 $cm^{-1}$ due to direct thermometer absorption.

Including light reflected from the light guide walls meant that these measurements have slightly distorted frequency dependence. From later experiments, it would be expected that focusing all the source radiation onto the sample would give a slightly stronger signal at higher frequencies. The increase in absorption with increasing frequency in the 100 $cm^{-1}$ to 400 $cm^{-1}$ range would be slightly more prominent in a carefully measured spectrum.

Looking for evidence of a superconducting gap, low frequency spectra were measured with both a white polyethylene filter at 77 K and a $^4$He temperature fluorogold filter. These filters cut out all significant background radiation, with a high frequency limit of 50 $cm^{-1}$ determined by the fluorogold filter at 4.2 K. In these measurements, the minimum sample temperature was 3 K, significantly below the 3.8 K superconducting transition temperature. Because the bolometer is operated at a very low temperature, the thermometer has relatively high sensitivity and there is a reasonable signal below 10 $cm^{-1}$, the frequency region where a superconducting gap should be observed.

Figure 2.24 shows a ratio of the spectra measured at temperatures of 3 K and 4.4 K, above and below the superconducting transition. There is no evidence of any significant change in the absorption characteristics, particularly in the low frequency region where a gap might appear in the optical absorption spectrum at a temperature below $T_c$.

From these experiments, it could be concluded that for $(BEDT-TTF)_2AuI_2$, there
Chapter 2. Bolometric Measurements

Figure 2.23: Absorption in the 100 cm$^{-1}$ to 350 cm$^{-1}$ region for (BEDT-TTF)$_2$AuI$_2$. Unlike the TTF – TCNQ spectrum, for this highly conducting material there are no phonon features in the far-infrared region.
Chapter 2. Bolometric Measurements

Figure 2.24: A ratio of the \((BEDT-TTF)_2AuI_2\) absorption measured at temperatures above and below \(T_c\) shows no significant change at the BCS gap energy, \(2\Delta = 9 \text{ cm}^{-1}\).
is not a dramatic drop in the absorption at energies below \( T_c \) in the frequency region of a BCS energy gap. If the traditional BCS–type optical response does occur, it would seem to be a very small effect which is buried beneath other absorption processes. There are several difficulties, associated with the low \( T_c \) of this sample, which put a limit on the conclusions which can be drawn from these experiments. The minimum sample temperature was not very far below \( T_c \), and the region of interest, below 10 cm\(^{-1}\), is in the range where the spectral signal is dropping away rapidly. Thus, the signal is weak and the magnitude of the expected effect is reduced due to the low temperature measurement being not far below \( T_c \). Measurements on a higher temperature superconductor could possibly alleviate these problems.

### 2.5.2 Bolometric Absorption of \((BEDT-TTF)_2[Cu(NCS)_2]\), With a Superconducting Transition at \( T_c = 10.4 \text{ K} \)

Using a sample with a higher transition temperature should make it much easier to observe the optical effects of the superconducting transition. With higher \( T_c \), the BCS gap energy moves to higher frequency, further away from the low frequency limit of our spectrometer. In addition, it is possible to measure spectra much closer to the \( T=0 \text{ K} \) limit, since a minimum sample temperature in the 4 K region is relatively low in comparison to \( T_c \). For the \((BEDT-TTF)_2[Cu(NCS)_2]\) sample with \( T_c=10.4 \text{ K} \), the BCS gap energy of \( 3.5k_BT_c \) should appear at about 25 cm\(^{-1}\).

\((BEDT-TTF)_2[Cu(NCS)_2]\) crystals used in these experiments were provided by Jack Williams, from Argonne National Labs. The largest crystals which we received had a highly conducting \( b-c \) plane surface with dimensions of about 0.15 cm \( \times \) 0.25 cm. Perpendicular to this plane, the poorly conducting \( a \) axis would be between .05 cm and .005 cm. The larger \( b-c \) surface was usually flat and shiny, although in some cases, there were several sections with slightly different orientations. At Argonne, other crystals
grown in the same batch as our sample were used in magnetic flux exclusion experiments to confirm the correct superconducting phase. In addition, a more detailed 3.4 GHz microwave surface impedance measurement, performed by Doug Bonn, showed a transition midpoint at about 10.5 K and fully developed superconductivity by 8 K.

As in the \((BEDT-TTF)_2AuI_2\) measurements, orientation of the crystalline axes was determined using the mid-infrared reflectivity. Despite the non-stacked arrangement of \(ET\) molecules giving relatively isotropic electrical properties, there is enough polarization dependence in the mid-infrared reflectivity to determine the orientation of the crystal.

Bolometric absorption measurements for \((BEDT-TTF)_2(Cu(NCS)_2)\) were carried out at temperatures both at and below the 10.4 K superconducting transition temperature. The experimental technique was similar to that used for the \((BEDT-TTF)_2AuI_2\) measurements. Presented here are the most recent measurements, which show the least amount of leakage radiation heating the thermometer directly, and at the same time have a reasonable signal/noise ratio. This bolometer's sensitivity and electrical noise characteristics have already been shown in Table 2.3. Comparing the \(NEP\) values for this detector at 10.5 K and 5.3 K, it is seen that the signal will be approximately 10 times noisier at the higher temperature. In this case, the decreasing sensitivity with increasing temperature prevented the maximum temperature from being set higher than 10.5 K.

Both the absence of spectral features characteristic of direct thermometer absorption, and the polarization dependence of the signal amplitude, demonstrated that sample absorption dominated the measured signal. The bolometric absorption was measured between 0 \(cm^{-1}\) and 380 \(cm^{-1}\) using both a 3 \(mm\) source aperture and a small 0.5 \(mm\) \(\times\) 0.75 \(mm\) rectangular aperture. The size of the rectangular aperture was set visually to focus the radiation directly onto the sample surface at a nearly normal angle of incidence, while the larger circular aperture allowed light to reflect from the light guide walls onto the sample at an oblique angle. In both cases, the spectra did not show the
360 cm\(^{-1}\) peak which indicates the presence of leakage radiation heating the thermometer directly.

Using both the large and small apertures, the absolute level of the absorption signal was measured as a function of the polarizer angle. Table 2.4 shows the results, demonstrating that for the smaller aperture the polarization dependence is similar to the instrumental ratio of 3:1 between angles of 0 and 90 degrees, but is distinctly different with the larger aperture. Since leakage radiation is independent of polarization, the polarization dependence of the signal measured with the larger aperture is a good indication of sample absorption. What is not immediately obvious however, is why there should be such a large difference in the polarization dependences measured with the two apertures. The best explanation lies in the fact that for the c polarization, light reflected from the sides of the light guide onto the sample is given a component polarized along the poorly conducting crystalline axis, while for \(\vec{E} \parallel b\), polarization is preserved. For \(\vec{E} \parallel c\), this incorporation of a strongly absorbed component leads to the relatively larger increase in signal with increased source aperture size. Comparison of the signals measured with the small and large source apertures helps to confirm this hypothesis. Only for the \(\vec{E} \parallel b\), which is preserved in the light guide reflections, does the extra light from the larger aperture increase the signal by a factor of three, as would be expected considering the geometry of the light guide. These considerations show that the polarization dependence of the absorption of the \((BEDT-TTF)\_2[Cu(NCS)\_2]\) crystal can only be accurately determined using the configuration with light focused directly onto the sample surface at normal incidence. Using this data, and taking into account the instrumental polarization, shows that the far-infrared optical absorption is nearly isotropic along the \(b\) and \(c\) axes.

On the first cooling cycle of the sample, spectra were measured without any cold spectral filters in front of the sample. A typical result shown in Figure 2.25. This spectrum was obtained by combining separate measurements covering the spectral regions
Table 2.4: Absorption as a function of polarizer angle was measured for two source aperture sizes using the \((BEDT-TTF)_2[\text{Cu}(NCS)_2]\) bolometer. With the small rectangular aperture, the light is completely focused onto the sample surface, while the larger aperture allows light to reflect from the light guide walls onto the sample.

<table>
<thead>
<tr>
<th>Polarizer Angle (degrees)</th>
<th>Focused Rectangular Aperture ((0.05 \times 0.075 \text{ cm}^2)) Signal (mV)</th>
<th>3 mm Circular Aperture Signal (mV)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ((\vec{E} \parallel b))</td>
<td>0.130 ± 0.010</td>
<td>0.325</td>
<td>0.40</td>
</tr>
<tr>
<td>10</td>
<td>0.115</td>
<td>0.350</td>
<td>0.33</td>
</tr>
<tr>
<td>20</td>
<td>0.105</td>
<td>0.375</td>
<td>0.28</td>
</tr>
<tr>
<td>30</td>
<td>0.095</td>
<td>0.385</td>
<td>0.25</td>
</tr>
<tr>
<td>40</td>
<td>0.080</td>
<td>0.375</td>
<td>0.21</td>
</tr>
<tr>
<td>50</td>
<td>0.070</td>
<td>0.340</td>
<td>0.21</td>
</tr>
<tr>
<td>60</td>
<td>0.060</td>
<td>0.30</td>
<td>0.20</td>
</tr>
<tr>
<td>70</td>
<td>0.045</td>
<td>0.25</td>
<td>0.18</td>
</tr>
<tr>
<td>80</td>
<td>0.040</td>
<td>0.22</td>
<td>0.18</td>
</tr>
<tr>
<td>90 ((\vec{E} \parallel c))</td>
<td>0.040</td>
<td>0.215</td>
<td>0.19</td>
</tr>
</tbody>
</table>

from \(0 \text{ cm}^{-1}\) to \(100 \text{ cm}^{-1}\) and \(100 \text{ cm}^{-1}\) to \(350 \text{ cm}^{-1}\), with the source intensity focused almost completely onto the sample surface in both cases. Light is polarized with \(\vec{E} \parallel \hat{b}\) and the resolution is \(4 \text{ cm}^{-1}\). During the measurements, the thermometer temperature was 5.5 K but, with the presence of room temperature background radiation, the sample was at a higher temperature. Based on measurements of the bolometer time constant, it was estimated the sample temperature was 2 K above the thermometer temperature. Thus, the actual sample temperature was approximately 7.5 K.

Comparison of the bolometric sample absorption in Figure 2.25 with the direct thermometer absorption, shown in in Figure 2.22, demonstrates that the amount of leakage radiation is very small. There is a very small rise at the \(360 \text{ cm}^{-1}\) thermometer absorption peak but this feature is not a prominent part of the spectrum. Thermometer absorption became more significant when a larger source aperture was used to allow extra
Figure 2.25: The absorption spectrum of $(BEDT-TTF)_2[Cu(NCS)_2]$ in the region from 20 cm$^{-1}$ to 360 cm$^{-1}$ shows no significant phonon features and only slowly decreasing absorptance at lower frequencies. The absolute level of the absorption shows no sign of approaching zero at $\tilde{v} = 0$. The fact that there is only a very small peak at 360 cm$^{-1}$ indicates that direct thermometer absorption has a very small effect on this spectrum.
reflections from the light guide walls onto the sample. Analysis of these spectra showed that at least 80% of the lower wavenumber signal was due to sample absorption while less than 20% might be due to radiation leaking around the sample to be absorbed by the thermometer directly.

Spectra consistent with the data shown in Figure 2.25 were measured using several different crystals. Absorbed intensity is smooth and has a small positive slope in the region from 100 cm\(^{-1}\) to 350 cm\(^{-1}\). As was the case with \((BEDT-TTF)_2AuI_2\), absorption does not appear to be approaching zero at zero frequency and there are no significant phonon absorption features. For the \(\vec{E} \parallel c\) polarization, a similar spectrum was obtained, having the same absolute level when light was focused directly onto the crystal. A factor of three gain in signal was obtained by increasing the size of the source aperture to allow light to reflect from the sides of the wedged light guide onto the sample. This changed the ratio of absorption for the \(b\) and \(c\) polarizations to approximately 1:2, as discussed earlier, and slightly distorted the wavenumber dependence. The spectra became nearly flat in the 100 cm\(^{-1}\) to 300 cm\(^{-1}\) region and increased rapidly in the region below 30 cm\(^{-1}\) where the smaller aperture diffracted much of the light out of the beam. Figure 2.26 demonstrates this diffraction effect by comparing the Golay background measurements with the two source apertures. Other than these effects on the overall wavenumber dependence, the \((BEDT-TTF)_2[Cu(NCS)_2]\) absorption spectra measured with the large and small source apertures were very similar, showing no significant phonon absorptions in spectra having noise/signal as low as ±3%.

Measurements covering the low wavenumber region from 5 cm\(^{-1}\) to 45 cm\(^{-1}\) were obtained with cold optical filters in front of the sample during the third cooling cycle. Because of the addition of cold filters in the beam path and the weaker signal in this low frequency region, it was necessary to use the larger source aperture to allow extra reflections onto the sample from the light guide walls. Raw power spectra measured at
Figure 2.26: The low wavenumber region of the Golay background spectra demonstrate the effect of diffraction at the source aperture. Using a small aperture, very little light in the region below 15 cm$^{-1}$ reaches the sample chamber.
temperatures of 10.5 K and 5.3 K are shown in Figure 2.27. Radiation is again polarized with $\vec{E} \parallel b$ and spectral resolution is $2 \text{ cm}^{-1}$. The two spectra superimposed for each temperature give an indication of the noise level in the measurements. Poor sensitivity at $T = 10.5$ K made it necessary to increase integration time and average several runs. A ratio of the spectra measured at and below $T_c$ is shown in Figure 2.28. The high temperature spectrum used in this ratio is an average of four spectra with a combined measuring time of about four hours.

These measured absorption spectra show neither a superconducting optical gap nor interesting phonon features. Power spectra measured below $T_c$ show that there is absorption below the predicted BCS gap of 25 cm$^{-1}$ and that there are no features in the ratio of spectra measured at temperatures at and below $T_c$ which could be associated in any way with the superconducting transition. Even though the high temperature measurement was not far above $T_c$, for any conventional superconductor, such as lead[107] or aluminum[82], formation of the energy gap leads to a distinct change in the absorption with this variation in temperature. It must therefore be concluded that the optical response of this organic superconductor is quite different than that of the conventional metallic superconductors.

2.6 Conclusions Drawn From Bolometric Measurements on Superconductors

For both the organic and ceramic types of superconductors used in these experiments, there is absorption at energies below the conventional BCS gap energy, and any effect of the superconducting transition is not easily observable. As discussed in Chapter 1, there are several possible cases in which the superconducting gap might be hard to observe and which might explain this result.

Anisotropy of the superconducting gap could play a role in both the organic and
Figure 2.27: \((\text{BEDT-TTF})_2(\text{Cu(NCS)}_2)\) absorbed power spectrum measured with cold filters removing all background radiation above 45 \(\text{cm}^{-1}\). No correction has been made for the instrumental background and two spectra have been superimposed at each temperature to show the approximate noise level. (a) \(T=5.3\text{ K}\) (b) \(T=10.5\text{ K}\).
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Figure 2.28: A ratio of the $(BEDT-TTF)_2(Cu(NCS)_2)$ absorbed power spectra shown in Figure 2.27, measured with temperatures at and below $T_c$. There is no significant change in the absorption spectrum to be associated with the superconducting transition. The superimposed dashed line shows a scaled version of the measurements from superconducting aluminum, choosing the temperature $T = 0.9 \, T_c$ to match microwave surface impedance measurements (see text)[82].
ceramic crystals. In both these types of superconductors, electron transport is mostly restricted to two-dimensional, highly conducting planes. These anisotropic electrical characteristics make it quite likely that the superconducting gap would also be anisotropic, having a value much smaller than the BCS value, or even zero, for some positions on the Fermi surface. For \((BEDT-TTF)_2[Cu(NCS)_2]\), an anisotropic gap might explain the wide variability in results of tunnelling measurements and the broad transition seen in the heat capacity. The optical response of a superconductor with an anisotropic gap will be quite different than the simple BCS picture. Absorption will not drop to identically zero at the BCS value of \(2\Delta\) because lower energy photons still carry enough energy to excite electrons across the reduced gap. The dramatic drop in the optical absorption would be expected to occur only below the energy corresponding to the minimum gap on the Fermi surface.

It is also possible that the organic superconductors are in the clean limit, which would make any sort of gap very difficult to observe experimentally. Other techniques which have been used to investigate the superconducting limit for the \((BEDT-TTF)_2[Cu(NCS)_2]\) superconductor are Shubnikov–de Haas and \(\mu^+SR\) measurements. The Shubnikov–de Haas effect provides a fairly direct measurement of the conduction electron scattering time and gives a clean limit result of \(\tau = (3 \pm 1) \times 10^{-12} \text{ sec}\) or \(1/\tau \approx 0.3k_bT_c = 2 \text{ cm}^{-1}[108]\). The \(\mu^+SR\) experiment measures the magnetic penetration depth of the superconducting state and, after making approximations for the electron effective mass and the area of the Fermi surface, can be used to derive a ratio of coherence length to electron mean free path[49]. The result, \(\xi_0/l \approx 2.7\), lies inside the dirty limit \((\xi_0 \gg l)\) but is very sensitive to the particular choices made in estimating the effective mass and Fermi surface area.
The third way to estimate the clean and dirty limits is through the normal state reflectivity measurements which will be discussed in the following chapter. From Kramers-Kroning analysis of the reflectance, the frequency dependence for the conduction electron response can be seen in the optical conductivity spectrum. Our measurements show a low frequency Drude-like conductivity peak with a half width of about 30 cm$^{-1}$, very close to the predicted BCS gap energy of 25 cm$^{-1}$.

Recent high-frequency microwave measurements might also play a role in explaining the lack of a change in the far-infrared absorption at temperatures above and below $T_c$. Surface resistance, which is directly proportional to the optical absorptance, has been measured using microwave techniques at a frequency corresponding to a wavelength of 3 cm$^{-1}$. The result, displayed in Figure 2.29, shows that at a temperature of $T = 0.5 T_c$, the surface resistance is only about 0.2 times the normal state value. At this temperature, the absorption of the superconducting state is far higher than both the prediction of the BCS theory, and a measurement on superconducting niobium. Our measurements cover a range of energy where the difference between superconducting and normal state absorptance should be even smaller, as can be roughly seen from the measurements on aluminum shown in Figure 1.37. The equivalent curve for aluminum, having a ratio of superconducting to normal surface resistances of 0.2 at an energy of 0.1$k_bT_c$, occurs at a temperature of $T \approx 0.9T_c$. A scaled version of this $T = 0.9 T_c$ data from Figure 1.37 has been superimposed on our data in Figure 2.28. This comparison shows that the difference between superconducting and normal surface resistances could be greatly reduced over a large part of the region below the gap energy, $2\Delta$. 

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Figure 2.29: Microwave surface impedance is much higher for \((BEDT-TTF)_2\text{Cu(NOCS)}_2\) than for either a Nb superconductor or the BCS calculation. This measurement was made at a frequency of about 3 cm\(^{-1}\), or 0.1\(k_B T_c\)[109].
Chapter 3

Reflectivity Measurements

Reflectivity measurements, covering the spectral region from 200 cm\(^{-1}\) to 6000 cm\(^{-1}\), were performed on the organic superconductor, \((BEDT-TTF)_2[Cu(NCS)_2]\). Both protonated and deuterated crystals were used in cryogenic measurements with temperatures varying from 300 K down to a minimum of 6.5 K. The low frequency spectral limit in these measurements includes a region of overlap with the bolometric absorption measurements between 200 cm\(^{-1}\) and 360 cm\(^{-1}\), but does not extend to a low enough frequency to look for effects of the superconducting transition directly. There are several important features of the measured optical response. Broad features in the mid-infrared region (1000 cm\(^{-1}\) to 3500 cm\(^{-1}\)) and sharp phonon features both exhibit interesting polarization and temperature dependences. In addition, at low temperature there is a dramatic increase in the reflectivity which is directly related to the metallic properties of the sample. Using the reflectivity measurements covering a wide frequency range, the important step of applying the Kramers–Kronig relations to derive the optical conductivity was performed. A brief summary of our work in this area can be found in several recent publications[110, 111].
3.1 Experimental Technique

3.1.1 Spectrometer

All the spectral reflectivity measurements were performed using a Bruker 113V spectrometer[54]. A ray diagram of the instrument as from above is shown in Figure 3.1. During measurements, the entire spectrometer volume is evacuated to remove unwanted water vapour absorption lines and to improve the general instrumental stability. In order to perform measurements of reflectance, the main modification to this instrument is the insertion of a reflectivity module into one of the sample chambers.

The Bruker spectrometer is directly interfaced with a computer to allow both data collection and analysis, and control of the instrumental configuration. Data is collected in a fast-scanning mode, with the scanning mirror position determined using a separate interferometer with a white light source and a Helium–Neon laser. The white light interferogram produces a peak at zero path difference which is used to initialize counting of the laser fringes. As the mirror moves, the infrared signal is digitized with points spaced appropriately to give the desired high frequency spectral limit. Each scan of the mirror typically takes a few seconds and several hundred interferograms are averaged before a Fourier transform is performed to derive the optical spectrum.

Measurements covering different spectral regions require specific choices of sources, beamsplitters, and detectors. With the Bruker spectrometer, these components can all be interchanged through various electrical motors and servo–mechanisms which are controlled through the computer. There is a choice of 3 sources, 4 source apertures, 6 beam–splitters, 4 optical filters, and four detectors. A fifth detector, a commercial far-infrared bolometer detector, operating at 4.2 K, sits on top of the instrument with a fixed mirror bringing the beam up from below. This mirror is positioned so as not to interfere with the operation of the two most important liquid–$N_2$ cooled detectors, but prevents
Figure 3.1: This ray diagram of a Bruker 113V spectrometer shows the general instrumental configuration. A computer interface allows automatic switching of sources, optical filters, beam-splitters, front and back sample chambers, and detectors. (A) Sources. (B) Filter wheel. (C) Beamsplitters. (D) Moving mirror. (E) Laser and white light interferometer. (F) Sample chambers. (G) Detectors.
use of the room temperature far-infrared and near-infrared detectors. The two sources used in these experiments are a mercury–arc lamp, providing a signal below 600 cm\(^{-1}\) and a globar covering the region from 400 cm\(^{-1}\) to 6000 cm\(^{-1}\). For the far-infrared region, mylar beam–splitters were used in combination with the 4.2 K bolometric detector, while in the mid-infrared region, KBr and CaF beamsplitters were used with photo–conductive MCT (mercury–cadmium–teluride) and photo–voltaic InSb detectors, both operating at 77 K.

3.1.2 Reflectance Module

The reflectance module, which is placed in one of the Bruker sample chambers, is shown in Figure 3.2. Source radiation comes to a focus on an adjustable rectangular aperture, which is imaged at the sample position using the first toroidal mirror. Incident angle at the sample surface is about 15 degrees. Using the visible light from the tungsten source, positions of the aperture and the first toroidal mirror are adjusted to produce a well focused image at the plane of the sample. The aperture has separate adjustments for both vertical and horizontal size and is set to have dimensions matching those of the sample. For the reflectivity measurements, the size is set to be slightly smaller than the sample, ensuring that the entire beam proceeding to the detectors has reflected from the area of the sample surface.

Light reflected by the sample is collected by a second toroidal mirror and fed back onto the original spectrometer beam path. Because it is impossible to mount the sample and reference surfaces with exactly identical orientation, there are vacuum feedthroughs to allow adjustment of the collecting toroidal mirror orientation. Each time sample and reference surfaces are exchanged, the detector signal is maximized to ensure that all the reflected light reaches the detector. The best results are obtained if only minor adjustments are required to re–maximize the signal when switching between sample and
Figure 3.2: The Bruker reflectance module viewed from the top[112]. (A),(B) Mirror and sample. (C) Radiation shield. (D) Vacuum shroud. (E) Polarizer. (F) Adjustable rectangular aperture. (G) Plane mirrors. (H) Toroidal mirrors. (I) Chopper. (J) Vacuum feedthrough to move chopper into the beam. (K) Sample chamber extension. (L) Plexiglass cover. (M) Direction of translation exchanging sample and reference surfaces.
reference surfaces. In the best cases, this optimization increases the signal by only a few percent.

Other important components of the reflectivity module are the chopper and the polarizer. Maximization of the reflected signal is most easily accomplished with the chopper in the beam and the detector signal monitored with either an ac voltmeter or a lock-in amplifier. Using the vacuum feedthrough shown in Figure 3.2, the chopper can be moved in or out of the beam while maintaining the instrument vacuum. Polarization of the beam is also important in measurements on the organic crystals for which the optical properties are not isotropic. Several different polarizers are required to cover the entire infrared region and are interchanged manually. The angle of the polarization can be adjusted using a mechanical vacuum feedthrough, with the angle set by visually aligning marks on the polarizer mounting ring.

Power reflectivity is measured by mounting the sample and a reference mirror side by side and interchanging the two surfaces in the beam. Both sample and reference surfaces are within the cryostat, which is mounted on a translating platform on the spectrometer lid as shown in Figure 3.3. The cold tip of the cryostat extends down from the lid to the level of the instrumental beam path. Turning a differential thread moves the mounting plate, with pins in slots guiding the movement and a sensitive dial-indicator monitoring the position. Using this system, sample and reference mirrors can be repeatedly interchanged, resulting in reflectivity spectra having reproducibility within ±0.5%.

3.1.3 Sample Mounting and Cryogenics

Figure 3.4 shows the Air Products Heli-tran liquid transfer cryostat (model LT-3-110) on which the sample was mounted for these experiments. Cold sample temperatures are maintained by a steady flow of either liquid nitrogen or helium from a pressurized
Figure 3.3: In order to exchange the sample and reference surfaces in the beam path, the cryostat is mounted on a plate on the lid of the interferometer sample chamber and is translated using a differential thread. Using this system to exchange sample and reference surfaces gives measured reflectivities which are reproducible to within ±0.5% [112].
Figure 3.4: The Air Products Heli-tran LT-3-110 cryostat uses a continuous flow of liquid helium or nitrogen to maintain cryogenic sample temperatures [113]. With some room temperature radiation coming in through the aperture in the radiation shield, the minimum sample temperature obtained was 6.5 K.
supply dewar to the cryostat. A portion of the liquid is diverted for cooling a heat shield in the transfer line, while the remainder goes directly to the cryogenic cold tip. A steady sample temperature above the minimum temperature can be maintained by restricting the flow of liquid to the cold tip, and using a computerized temperature controller (Scientific Instruments Series 5500) to provide current to an electrical heater. This system is capable of controlling the temperature to within 0.4 K for temperatures between 6 K and 300 K. At the minimum temperature, liquid $^4$He is consumed at a rate of about 1 litre per hour.

A copper radiation shield, with an aperture allowing the spectrometer beam to reflect from the sample, protects the cold tip from external room temperature radiation. Factory-installed diode thermometers mounted on the cold tip indicated a minimum temperature of 4.8 K. With room temperature radiation passing through the hole in the radiation shield, the minimum sample temperature was between 2 K and 8 K higher, depending on the particular sample mounting arrangement. Because reflectivity measurements were performed in the mid-infrared region where the background radiation is most intense, any cold filter which would be effective in blocking background radiation would also prevent the spectrometer radiation from reaching the sample. For this reason, no cold filters could be used in these experiments.

The vacuum shroud separating the high-vacuum cryogenic region from the spectrometer included an infrared window of either polypropylene or CsI. Both these types of window are transparent to visible light, allowing location of the spectrometer beam within the cryostat by eye. The polypropylene window is made from a 50 $\mu$m thick sheet, and transmits in the far-infrared region below about 600 $cm^{-1}$. A 3 mm thick polished crystal of CsI is used for the region above 200 $cm^{-1}$. Because of the small size of the sample, diffraction effects limited the useful spectra to the region above 100 $cm^{-1}$. Below this frequency, the signal was much smaller and accuracy was distorted with a
gradual decrease in the measured reflectivity spectrum. For this reason, most of the measurements at cryogenic temperatures were made using the region above 200 cm$^{-1}$.

The mount used to hold the sample and reference mirror is shown in Figures 3.5 to 3.7. A clean evaporated aluminum-on-glass mirror was used as the reference. This mirror was cut from a commercially produced plane mirror which comes with a plastic protective coating which was removed shortly before mounting of the mirror. A spring clip and epoxy glue held the mirror in place. Gold wires were used to suspend the sample next to the reference mirror. This arrangement allowed almost all of the small reflecting surface (typically 0.1 cm$\times$0.2 cm) of the organic single crystal sample to be used. Many strands of 0.0025 cm diameter gold wires supporting the sample helped bring the temperature close to the temperature of the cryogenic cold tip. The coldest sample temperature in these experiments was obtained using 48 strands of wire, although in most cases between 5 and 10 strands were used.

A doped silicon thermometer, similar to those used for the bolometric absorption measurements, was glued to the back of the sample to determine the temperature. Measurement of the actual sample temperature was ensured by using brass alloy electrical leads, which have low thermal conductivity, for the thermometer. The operating range of the doped silicon thermometer is below 30 K, and showed that the minimum sample temperatures were between 6.5 K and 12 K for the different crystals used in these measurements.

Assembly of the various parts making up this sample mount was done in a sequence minimizing the possibility of damage to the delicate parts such as the sample and the thermometer. All the external electrical wiring was done first, including the soldering of the fine brass leads which were later connected to the thermometer. Then the gold support wires were strung across the gap in the mount and glued in place. After this, the more delicate step of connecting the thermometer was undertaken. A working platform
Chapter 3. Reflectivity Measurements

Reflectance Mount – Front View

1. Copper mount
2. Reference mirror
3. Sample (supported by gold wires)

Reflectance Mount – Rear View

1. Copper mount
2. Reference mirror
3. Sample
4. Gold wires
5. Thermometer
6. Brass leads
7. Solder points

Figure 3.5: Schematic diagrams showing front and rear views of the sample mount used for the reflectivity measurements. The sample and an evaporated aluminum on glass reference mirror are side by side, with the sample suspended on gold wires. A doped silicon thermometer is glued to the back of the sample and is sensitive at temperatures below 30 K.
Figure 3.6: Photographs of the reflectivity sample mount as viewed from the front and rear.
Figure 3.7: Close-up photographs of the deuterated $(B E D T-T T F)_2[C u(N CS)_2]$ sample mounted for reflectivity measurements.
was set in the place where the sample would sit, and the thermometer leads were bent to positions where they would be in contact with the electrical contacts on the thermometer. Then the thermometer was carefully moved into place and the electrical wires bonded using conducting epoxy. When the glue had set, the sample mount was raised above the working platform, the sample put into the desired position, and, with epoxy applied to the appropriate surfaces, the mount was lowered back down so that the support wires and thermometer were in contact with the sample. The sample mount was clamped in this position and set aside for 24 hours while the glue hardened.

Suspension of the sample on flexible gold wires was a useful feature of this sample mount because it allowed for some fine tuning of the sample surface orientation. Before mounting the sample holder on the Heli-tran cold tip, the assembled mount was placed on a translating table and the light from a Helium–Neon laser was reflected from either the sample or reference surface. Observing the position of the spot reflected onto a screen about 1 m away, fine adjustments of the sample orientation were made until alignment with the reference mirror was achieved.

One fairly important part of the sample mount, which is not shown in Figure 3.5, is a small piece of white painted copper located beside the reference mirror. After the cryostat was on the spectrometer, the reflectance module optics were set up using the visible component of the near-infrared beam. Looking at the focused image of the aperture on this white screen, both the sharpness and the size of the aperture could be accurately set to focus light completely onto the sample area.
3.2 Large Picture–R and $\sigma$ as a Function of Temperature

Reflectivity measurements were performed using three different protonated crystals and one deuterated crystal. In all cases, the reflectance was measured as a function of temperature, with the best results used for Kramers–Kronig analysis to derive the optical conductivity. For this analysis, the accuracy of the low temperature measurements is very important, and so an absolute calibration procedure was developed to correct for any systematic error which might affect the low temperature measurement.

3.2.1 Room Temperature Measurements

Extensive room temperature measurements were carried out for each sample before performing any cryogenic experiments. In these measurements, the accuracy and reproducibility of the experimental technique could be tested without the added complication of maintaining the sample at cryogenic temperatures. The most important requirement to satisfy was that the reflectivity should not be affected in any significant way by the particular instrumental configuration used. Absolute reflectance should agree in the overlapping regions for different spectral ranges, and it should not be affected by either installation of a purge window on the cryostat vacuum shroud, or by limiting the beam to a smaller portion of the sample surface.

These room temperature experiments showed the importance of having accurately aligned sample and reference surfaces. Overlap of the different spectral regions was especially susceptible to any misalignment, since the far-infrared bolometer and the mid-infrared MCT detectors have quite different light collecting characteristics. The bolometer has a light guide system bringing in light from a large area while the MCT detector has an ellipsoidal mirror focusing the beam directly onto a very small detector area. If either the sample or reference surface is misaligned, light will be poorly focused
onto the mid-infrared MCT detector, while it is still almost completely collected by the bolometer light pipe optical system. In cases where there is disagreement between the far and mid-infrared regions, the problem usually lies in the mid-infrared spectrum. The level of the mid-infrared measurement can be brought into agreement with the far-infrared by carefully aligning the sample and reference surfaces using the Helium-Neon laser.

Figure 3.8 shows the region of overlap between the mid and far-infrared \((\text{BEDT-TTF})_2[\text{Cu(NCS)}_2]\) reflectivities at room temperature. Absolute reflectivities in the overlapping region agree to within \(\pm 1\%\). Similar agreement, shown in Figure 3.9, can be achieved between the mid and near-infrared regions. When this level of accuracy is reached, any spectrometer changes, such as using a smaller area of the sample surface, interchanging polarizers, or inserting the room temperature cryostat vacuum shroud, do not have any impact on the measurement.

These measurements produce consistent results not only using different detectors and a single sample, but also among different samples. Room temperature measurements on the three protonated samples all display absolute reflectivities within the \(\pm 1\%\) uncertainty between the overlapping regions. These measurements are also in complete agreement with other published room temperature measurements\(^{[16, 67, 70]}\). From these high levels of reproducibility, it is concluded that room temperature reflectivity can be measured to within an accuracy of 1\% for samples of \((\text{BEDT-TTF})_2[\text{Cu(NCS)}_2]\) smaller than 0.1 cm \(\times\) 0.2 cm between 200 cm\(^{-1}\) and 6000 cm\(^{-1}\).

The complete room temperature spectra, in which the measurements covering different spectral regions have been merged, are shown in Figure 3.10. There are significant differences between the \(\vec{E} \parallel b\) and \(\vec{E} \parallel c\) spectra, although the general shapes and absolute levels are similar. For both polarizations, the reflectivity approaches a value between 0.5 and 0.55 in the far-infrared. In order to perform the Kramers–Kronig analysis, the
Figure 3.8: Overlapping region between far and mid-infrared $(BEDT-TTF)_2[Cu(NCS)_2]$ reflectivity spectra. At room temperature, agreement within ±1% is achieved after ensuring good alignment of sample and reference surfaces.
Figure 3.9: Overlapping region of the mid and near-infrared \((BEDT-TTF)_2[Cu(NCS)_2]\) reflectivity spectra.
reflectivity below 100 cm\(^{-1}\) was extrapolated smoothly to 1.0 at \(\tilde{\nu} = 0\).

Figure 3.11 shows the derived optical conductivity. For both polarizations, the spectra are dominated by a broad hump in the mid-infrared. This feature is most likely due to direct transitions between allowed electronic energy bands, as demonstrated by the band structure shown in Figure 3.12. This band calculation has been confirmed through agreement with both thermopower and Shubnikov–de Haas results, and shows that the available states are separated from the filled levels by energies ranging from nearly zero to 0.6 eV (4800 cm\(^{-1}\)). Optical absorption due to these direct interband transitions would be expected in this entire energy range. The detailed calculations which would be required to convert from this band structure to an optical absorption spectrum have not yet been performed. However, one qualitative observation which can be made is that the peak in the spectrum should appear at an energy somewhere below the maximum band separation, since the probability for transitions decreases inversely with increasing gap energy. Thus, the observed peaks in the 2200 cm\(^{-1}\) to 3200 cm\(^{-1}\) range could very well result from the full analysis of the band structure.

3.2.2 Low Temperature Measurements, and Scaling of Absolute Reflectivity using Bolometric Absorption

A broad picture of the temperature dependent mid-infrared reflectivity is shown in Figures 3.13 and 3.14. In the temperature range below 100 K, the reflectivities for both polarizations show similar temperature dependence, pivoting around a point in the mid-infrared at about 2200 cm\(^{-1}\). In the low frequency region below 2000 cm\(^{-1}\), there is a dramatic increase in the reflectivity, while in the higher frequency region there is a slight decrease with decreasing temperature.

Unfortunately, the absolute reflectance levels measured at low temperature have relatively large uncertainties. Figure 3.15 shows the mid-infrared reflectivities measured for
Figure 3.10: $(\text{BEDT-TTF})_2[\text{Cu(NCS)}_2]$ room temperature reflectivities for $\vec{E} \parallel b$ and $\vec{E} \parallel c$ have similar shapes and magnitudes. This isotropic response is characteristic of the samples' two-dimensionality. For a one-dimensional organic conductor, a spectrum with a similar shape is measured for the polarization along the highly conducting axis, while the perpendicular polarization has reflectivity reduced by a factor of more than 2.
Figure 3.11: Kramers–Kronig analysis of the reflectivity gives the optical conductivity of $(BEDT-TTF)_2[Cu(NCS)_2]$. The main feature is the broad hump covering most of the mid-infrared region, which is centred within an energy range where band structure calculations show possible electronic transitions.
Figure 3.12: The calculated band structure shows allowed electronic transitions between the filled and empty bands at energies ranging from nearly zero up to 0.6 eV (4800 cm$^{-1}$). In addition to these interband transitions, there are many possible intraband transitions in the energy range down to 0 eV. The zero of the energy scale in this figure corresponds to the ionization potential for an electron from the conducting ET plane[38].
Figure 3.13: \((BEDT-TTF)_2[\text{Cu(NCS)}_2]\) mid-infrared reflectivities measured at temperatures of 8.5 K, 30 K, 50 K, and 100 K, for the polarization \(E \parallel b\).
Figure 3.14: \((\text{BEDT-TTF})_2[\text{Cu(NCS)}_2]\) mid-infrared reflectivities measured at temperatures of 8.5 K, 30 K, 50 K, and 100 K for the polarization, \(\vec{E} \parallel c\).
the three different \((BEDT-TTF)_{2}[Cu(NCS)_{2}]\) crystals, with the sample at the minimum temperature in each case. For all three samples, two measurements at the same temperature gave results reproducible to within ±0.5%. While polarization and wave-number dependences of the spectra are in good agreement, the absolute values vary by 10% between the maximum and minimum results. In two of the three measurements, the mid-infrared spectrum is definitely too high, as will be seen by comparison with the far-infrared part of the spectrum.

An additional complication which makes these measurements even more difficult is the change in optical response with thermal cycling. Figure 3.16 shows the far-infrared part of the spectrum measured using the deuterated sample in three consecutive cooling cycles. For both polarizations, the measured reflectivity decreases quite significantly, especially by the third cooling. The decrease is slightly larger for the \(\vec{E} \parallel c\) polarization than for \(\vec{E} \parallel b\), possibly indicating development of microscopic cracks, with a preferred direction along one of the crystal axes. To minimize the influence of thermal cycling, all the spectra discussed here were obtained on the first cooling of the sample.

Sample size limitations allowed far-infrared measurements on only two of the three protonated samples, and in both of these cases the overlap with the mid-infrared region was not good. The mid-infrared level was about 5% higher than the far-infrared in both experiments, indicating some problem with the experimental technique at low temperature. Spectra measured using the first sample are shown in Figure 3.17. In this case, the mid-infrared region is clearly too high since scaling up the far-infrared to match would push \(R\) above 1.0. The measured far-infrared reflectivity might be accurate, however, considering both the low sensitivity of the bolometer to misalignment (compared to the MCT detector) and the good agreement with the only other published low-temperature mid-infrared spectrum[16]. Direct reflectivity measurements using the third sample were even less reliable. Both the far and mid-infrared reflectivities were about 4% higher.
Figure 3.15: Mid-infrared reflectivities measured for three different \((BEDT-TTF)_2-[Cu(NCS)_2]\) samples at low temperature do not agree very well. Systematic problems, which do not affect the room temperature measurements, cause variations in the measured reflectivity levels at low temperature (diagram continued on next page).
Figure 3.15: Continued.
Figure 3.16: The far-infrared reflectivity of deuterated \((BEDT-TTF)_2[Cu(NCS)_2]\) drops significantly with thermal cycling.
than measured with the first sample, with the lowest temperature far-infrared level at $R = 1.02$ in the region between $200 \text{ cm}^{-1}$ and $300 \text{ cm}^{-1}$.

The best explanation for this relatively poor accuracy of the low temperature data is that some distortion of the reference mirror leads to a poor image at the detector during the background measurements. Such an effect could be brought about by the different thermal contractions of the glass mirror substrate and the copper mount. Simple misalignment due to a shift in the reference mirror orientation is not likely, since maximization of the signal intensity did not require any large adjustment of the second toroidal mirror at low temperature.

From our low temperature measurements on the two larger samples, the only reasonable results came from the first sample in the far-infrared. The other far-infrared measurement and both of the mid-infrared measurements were clearly too high. Using the second sample, which was about half the size of the other two, only the mid-infrared region was accessible. This low-temperature mid-infrared spectrum turns out to be in agreement with the one reasonable far-infrared measurement.

At these low temperatures, where the reflectivity of the organic sample is relatively high, measurement accuracy is important. A small displacement of the absolute scale can easily lead to incorrect features in the derived optical conductivity spectrum. Better accuracy from our measurements is certainly desirable, since the only other basis for judging the accuracy is through comparison with one other set of published data[16]. For this reason, a new technique was developed to correct for any systematic experimental errors and set an absolute scale for the reflectivity.
Figure 3.17: At low temperature, there is a significant mismatch between measurements covering the far and mid-infrared frequency regions. The better data from the two far-infrared measurements is shown here, with the mismatch between regions being about 5%.
Using Bolometric Absorption Measurements to Determine Absolute Reflectivity

An innovative method for accurately setting the absolute scale of the reflectivity was developed by combining the reflectivity measurements with a bolometric measurement. Using the thermometer glued to the back of the sample to measure the absorption signal bolometrically allowed simultaneous measurement of $R$ and $A$ within the Bruker reflectivity apparatus. Knowledge of the polarization dependence of both the inaccurately scaled version of the reflectivity and the absorption allowed derivation of a correction factor to set the absolute reflectivity scale. This calibration procedure eliminates any systematic errors in the experimental technique which affect the absolute level of the reflectivity, and has the potential to be applied to any sample having a polarization dependent optical response. As far as we are aware, these are the only measurements in which a bolometric absorption signal and a reflectance signal have been measured simultaneously on a single sample.

The sample on which these measurements were performed was unusually thick ($\approx 0.005 \text{ cm}$), so a significant thermal connection to the mount was required to obtain a reasonable response time constant. Sample support was through 48 strands of 0.0025 cm diameter gold wire, resulting in a low sample temperature and a fast response time, but relatively poor bolometric sensitivity. With no cold filters and mid-infrared source radiation incident on the detector, the measured sample temperature was 6.4 K. A short time constant partially made up for the poor sensitivity by allowing absorption measurements in the mid-infrared, where source intensity is much stronger than in the far-infrared. The absorption signal was measured up to $3500 \text{ cm}^{-1}$, where the rapid scanning interferometer modulates the signal at a frequency of about 800 Hz.

The bolometrically measured absorption signal is the product of three terms: the
incident radiation spectrum, \( I(\bar{\nu}) \), the frequency dependence of the bolometric response, \( S(\bar{\nu}) \), and the actual sample absorptance, \( A(\bar{\nu}) \):

\[
\text{Signal}(\bar{\nu}) = I(\bar{\nu}) \times S(\bar{\nu}) \times A(\bar{\nu}).
\] (3.1)

\( I(\bar{\nu}) \) is the spectrum which would be measured by an ideal detector (with a perfectly flat spectral response) placed at the sample position. The bolometric response, \( S(\bar{\nu}) \), is a function which decreases with wavenumber, since the signal drops quickly when the fast-scanning mirror modulates the intensity at a rate higher than the bolometric response time constant.

Lacking knowledge of both \( I(\bar{\nu}) \) and \( S(\bar{\nu}) \), the analysis was based on the polarization dependence of the measured absorptance. The reflectance module shown in Figure 3.2 was modified to place the polarizer in the beam before the sample. Sample absorptance was then measured for the two perpendicular polarizations along the crystallographic \( b \) and \( c \) axes. To compensate for the instrumental beam polarization, the sample spectra were divided by the appropriate reference mirror background spectra, measured with the MCT detector. The resulting absorption spectra have arbitrary scaling, correct polarization dependence, and distorted frequency dependence. In particular, the frequency dependence is affected by both the bolometric time constant reducing the signal at high frequency, and the MCT response dropping off at low frequency. Figure 3.18 shows the resulting absorption spectra, measured with 2 \( \text{cm}^{-1} \) resolution in runs lasting 30 minutes each.

In order to eliminate the distorted frequency dependence of these spectra, a ratio of the absorptions measured for the two polarizations is taken. This ratio can be compared to the polarization dependence of the reflectivity using the fact that \( A = 1 - R = 1 - x R_{\text{meas}} \). The factor, \( x \), is a correction factor to be applied to the measured reflectivity, \( R_{\text{meas}} \), which
Figure 3.18: Absorption of the \((\text{BEDT-TTF})_2[\text{Cu(NCS)}_2]\) crystal can be measured in the mid-infrared using the bolometric technique. The polarization dependence closely parallels that seen in the reflectivity, and can be used to set an absolute scale to the reflectance.
was clearly too high. The ratio for the \( b \) and \( c \) polarizations then becomes:

\[
\frac{A_b}{A_c} = \frac{1 - R_b}{1 - R_c} = \frac{1 - xR_{b,\text{meas}}}{1 - xR_{c,\text{meas}}},
\]

and \( x \) is adjusted to obtain agreement between the experimentally measured absorption and reflectivity. In anticipation of the experimental results, it is useful to note that the scaling factor, \( x \), is a number close to 1.0, and a first order expansion of the ratio 

\[
\frac{[1 - xR_{b,\text{meas}}]/[1 - xR_{c,\text{meas}}]}{R_{b,\text{meas}}/R_{c,\text{meas}}}
\]

\[
\approx \frac{1 - xR_{b,\text{meas}}}{1 - xR_{c,\text{meas}}} \left( 1 - x \right) \frac{R_{b,\text{meas}} - R_{c,\text{meas}}}{[1.0 - R_{c,\text{meas}}]^2}.
\]

Adjustment of the scaling factor to obtain agreement with the ratio \( A_b/A_c \) will clearly be most sensitive in a region where \( R_{b,\text{meas}} \neq R_{c,\text{meas}} \), and where \( R_{c,\text{meas}} \) is close to 1.0. For this \( (BEDT-TTF)_2[Cu(NCS)_2] \) sample, both these conditions occur in the region around the 1300 cm\(^{-1}\) phonon feature.

In taking a ratio of the bolometric absorption signal with the background spectrum measured using the MCT detector, the assumption is made that the polarization dependence measured for the reference signal is the same as that of the beam incident on the sample. Two instrumental effects could make this assumption invalid. Either the detector itself could have polarization dependent sensitivity, or the reflections from mirrors between the sample chamber and the detector (which are at non-normal angles of incidence) could diminish the intensity of one polarization compared to the other. The fact that the background measurements have the correct polarization dependence is demonstrated by comparing the measurements of reflectance and absorptance in the region between 700 cm\(^{-1}\) and 1100 cm\(^{-1}\). Figure 3.15 shows that in this region the absolute reflectivity drops by about 35% from above 0.90 down to about 0.60, and, apart from the narrow phonon features, the absolute reflectivities for both polarizations are identical. This means that the ratio between the polarized absorptances, divided by the
appropriate instrumental backgrounds, should be identically 1.0. The experimentally observed ratio of \( A(b)/A(c) \) in this region is flat and identically 1.0 to within the accuracy of the absorption measurement. This agreement between the reflectivity and absorptance measurements could only be achieved if the MCT background measurements have the same polarization dependence as the spectrum incident on the sample.

Now, Equation 3.2 can be used to obtain the scaling factor, \( x \), required to bring the measured reflectivity to the correct level. Adjustment of the correction factor is most sensitive in the region around the 1300 cm\(^{-1}\) phonon feature. Figure 3.19 shows the ratio between polarized absorptions superimposed on the reflectivity ratios for several values of \( x \). The best fit in the 1300 cm\(^{-1}\) region gives the scaling factor, \( x = 0.915 \pm 0.015 \).

In Figure 3.20, the results from the three protonated samples which were cooled to cryogenic temperatures are superimposed. For sample 1, the mid-infrared reflectivity level was scaled to match with the far-infrared measurement, giving good agreement with other published results. Sample 2 was too small to obtain far-infrared measurements and the raw mid-infrared data is shown here, without any scaling correction. For sample 3, the scaling was corrected using the measured mid-infrared bolometric absorption in the procedure outlined above.

Using these scaling procedures, the data from the three crystals is brought into good agreement. Above 750 cm\(^{-1}\), the three spectra overlap within ±1%. At lower frequencies however, the results from the first and third samples are significantly different. The measured reflectivity for one of the samples rises more steeply between 750 cm\(^{-1}\) and 500 cm\(^{-1}\), but then remains at a fairly constant level for lower frequencies. This is quite different from the response of the first sample which showed a smoothly increasing curve in this frequency range. This difference might be partially due to the lower temperature obtained in the third measurement. Measurements in the temperature range between 15 K and 30 K showed that it is not directly related to the superconducting transition.
Figure 3.19: A good fit is obtained between the ratio of polarized absorptances and reflectivities by applying a constant scaling factor to the reflectivities. The fit is especially sensitive in the region of the 1300 cm\(^{-1}\) feature where the scaling correction for the reflectivity can be found within ±1.5%.
Figure 3.20: The lowest temperature measurements for the three different protonated \((\text{BEDT-TTF})_2[\text{Cu(NCS)}_2]\) samples are shown here. For the first sample, the mid-infrared region was scaled down to match with the far-infrared, while for the second sample no scaling has been applied. The absolute level for the third sample was set using the mid-infrared bolometric absorption measurement.
Reflectivity Extrapolations

Before performing the Kramers–Kronig analysis of the measured reflectivity, it was necessary to extrapolate the data at both low and high frequencies. The high frequency extrapolation was made by fitting a Drude-function in the 3500 cm\(^{-1}\) to 5000 cm\(^{-1}\) region, where \(R\) is dropping quickly to the minimum. At frequencies beyond the measured region, this extrapolated reflectivity is similar to the published higher-frequency low-temperature data, where a slowly increasing reflectivity is observed[16].

The low frequency limit of most of the reflectivity measurements was determined by the 200 cm\(^{-1}\) cutoff of the CsI cryostat purge window. For the lowest temperature measurements, the far-infrared bolometric absorption data (from Chapter 2) was used to extend the measured region down to about 30 cm\(^{-1}\). The absolute level of the measured absorption was set so that \((1 - A_{\text{bol}})\) would merge smoothly onto the reflectivity. The low frequency region in Figure 3.20 includes this low frequency bolometric absorption data. For all other temperatures, the extrapolation started at the low frequency limit of the reflectivity measurements. In all cases, a smooth curve with frequency dependence, \((1 - R) \propto \nu^{1/2}\), was used to bring the reflectivity up to 1.0 at \(\nu = 0\). Lower frequency reflectivity measurements, performed using the polypropylene cryostat purge window, confirmed the shape of these extrapolations. The measurements also served to confirm the bolometric absorption results, showing no significant phonon features in the frequency region between 80 cm\(^{-1}\) and 200 cm\(^{-1}\).

Low Temperature Optical Conductivity

These experiments have produced an absolutely scaled reflectivity, with a level of uncertainty low enough that the important features in the derived conductivity spectrum are conclusively demonstrated. Using the low temperature reflectivity of the first sample
gave the optical conductivity shown in Figures 3.21 and 3.22. The mid-infrared frequency range still shows the broad peaks which are present at room temperature. At low frequency, however, there is a steep rise in the optical conductivity.

Optical conductivity as a function of temperature is shown in Figures 3.23 and 3.24. For both the polarizations, the low frequency conductivity peak shows similar behaviour, rising dramatically as the temperature is reduced. There is a factor of 2 uncertainty in the spectra below 200 cm$^{-1}$ due to the difference in spectra measured with different samples, the setting of the absolute reflectivity scale, and the extrapolation to low frequency. Despite these uncertainties, there is good agreement between the intercepts at $\nu = 0$ and measured dc conductivities. For both polarizations, the zero frequency intercepts are similar, increasing from about 35 (Ωcm)$^{-1}$ at 100 K, to 150 (Ωcm)$^{-1}$ at 50 K, and 1300 (Ωcm)$^{-1}$ at 25 K. The $T = 12$ K data in Figure 3.21 shows a further increase to a value close to 3000 (Ωcm)$^{-1}$, with the conductivity peak having a half-width of about 40 ± 15 cm$^{-1}$. These results are in agreement with the measured dc conductivity, an example of which is reproduced in Figure 1.14. These particular dc measurements show the commonly observed temperature dependence for (BEDT–TTF)$_2$[Cu(NCS)$_2$], although the level of conductivity is factor of 2 or 3 lower compared to most other results.

While the low frequency conductivity peak is showing this dramatic increase, the mid-infrared features show a corresponding decrease. This is due to the fact that the electrons contributing to the far-infrared conductivity peak are involved in intraband transitions, and are thus are no longer available for participation in the mid-infrared interband transitions. The conductivity sum rule requires that the total area under the conductivity curve should be constant, as long as both the number density and effective mass of charge carriers remains constant[114]:

$$I_\sigma = \omega_p^2 = \frac{2}{\pi} \int_0^\infty \sigma(\nu) d\nu$$
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Figure 3.21: Optical conductivity of \( (BEDT-TTF)_2[Cu(NCS)_2] \) is obtained from the reflectivity using Kramers-Kronig analysis. The main feature of the room temperature measurement, the broad hump in the mid-infrared, is still present at low temperatures. Low temperature metallic behaviour of the sample is seen only in the low frequency region below about 500 cm\(^{-1}\).
Figure 3.22: Optical conductivities measured at 295 K and 12 K superimposed the two polarizations. In the $\vec{E} \parallel b$ spectra, there is a shift in the position of the mid-infrared band with temperature, while for $\vec{E} \parallel c$ the feature is stationary.
Figure 3.23: The $\vec{E} \parallel b$ optical conductivity of the deuterated crystal has been derived from the reflectivities measured at temperatures of 100 K, 50 K, and 25 K. As a function of temperature, the zero frequency conductivities obtained by extrapolation produce reasonable agreement with the published dc conductivity measurements.
Figure 3.24: Optical conductivity of deuterated \((BEDT-TTF)_{2}[Cu(NCS)_{2}]\) at temperatures of 100 K, 50 K, and 25 K, for \(\vec{E} \parallel c\) polarized light.
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\[ = \frac{4\pi ne^2}{m}. \]  

Analysis of this equation will be considered in more detail in an upcoming section of this thesis.

In order to give a rough indication of the accuracy of the observed low frequency conductivity peak, the lowest temperature \( E \parallel b \) conductivity spectra measured for samples 1 and 3 (see Figure 3.20 for the reflectivity spectra) are shown in Figure 3.25. In both cases, the high level of the reflectivity leads to a conductivity peak with a zero frequency intercept more than an order of magnitude above the level in the mid-infrared region. For sample 3 however, the higher reflectivity in the 200 cm\(^{-1}\) to 600 cm\(^{-1}\) region contributes to a larger conductivity peak, with a zero frequency intercept of approximately 7000 (\( \Omega \text{cm} \))\(^{-1}\). Compared to this difference observed with different samples, the choices made in the far-infrared extrapolation have a relatively small impact on the shape and magnitude of the low frequency conductivity peak.

3.2.3 Fits with the Phase–Phonon and Drude–Lorentz Models

Calculation of the electronic band structure is the only fundamentally correct way to approach the theoretical derivation of the optical spectrum. A calculation of the optical conductivity, \( \sigma \), from the band structure requires knowledge of all the transition probabilities for the complete set of all interband and intraband transitions, and has not been performed, either for this material or for any other, as far as we are aware.

Starting from the band structure picture, several general predictions can be made. As has already been discussed, interband transitions will contribute to absorption throughout the mid-infrared region. In addition, the position of the mid-infrared peak would be expected to move to higher frequency with thermal contraction of the lattice since contraction in real space leads to expansion of the Brillouin zone. In a simple picture,
Figure 3.25: Low frequency conductivity peak compared for two ET samples at low temperature. The higher reflectivity in the 200 cm$^{-1}$ to 600 cm$^{-1}$ region for sample 3 (see Figure 3.20) leads to an increase in the magnitude of the low frequency conductivity peak.
this expansion causes an increase in the energy separation between bands. For \((BEDT-TTF)_2[\text{Cu(NCS)}_2]\), there is large thermal contraction between room temperature and 100 K, with the magnitude about 5 times larger along the \(c\) axis than along \(b\). From this simple picture, it might be expected that the peak in the \(\vec{E} \parallel c\) spectrum would show more change with temperature, while in fact Figure 3.22 shows that it is the \(\vec{E} \parallel b\) measurement which exhibits greater temperature dependence. It is likely that the full band structure calculation will have to be performed to fully explain these features.

In the absence of the complete band structure analysis, various models have been used to produce spectra similar to those measured for the organic conductors. In particular, the Drude–Lorentz model and the phase–phonon model have both produced curves which match the observed spectrum reasonably well\([16, 67]\). It should be emphasized, however, that neither of these models are based on a premise consistent with the calculated band structure. In both cases, the calculations start with either one or several semiconducting electronic transitions. This is completely different than the band calculations which show an almost continuous range of possible electronic transitions throughout the mid-infrared. Thus, while the models give fairly good agreement with the experiment, the premises on which they are based have little relationship to the actual physical processes in the material.

**Drude–Lorentz Model**

A reasonable fit with the observed conductivity can be obtained using the simple Drude–Lorentz model, as outlined in Chapter 1. Referring to Equation 1.27, the parameters which simulate the low temperature \(\vec{E} \parallel b\) measurement are shown in Table 3.1, with the resulting spectrum in Figure 3.26. A good fit requires two strongly damped Lorentz terms in the mid-infrared, a broad Drude term giving the low frequency strength up to 1200 \(cm^{-1}\), and a second Drude term giving the narrow dc conductivity peak. A narrow
Table 3.1: Parameters for the Drude–Lorentz model which fit the low temperature $\vec{E} \parallel b$
data.

<table>
<thead>
<tr>
<th></th>
<th>$\omega_{pi}(cm^{-1})$</th>
<th>$\omega_{o1}(cm^{-1})$</th>
<th>$\gamma_i(cm^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mid-infrared band</td>
<td>5660</td>
<td>2260</td>
<td>3600</td>
</tr>
<tr>
<td>Mid-infrared band</td>
<td>3550</td>
<td>3800</td>
<td>1370</td>
</tr>
<tr>
<td>Phonon feature</td>
<td>750</td>
<td>1340</td>
<td>40</td>
</tr>
<tr>
<td>Drude term</td>
<td>3420</td>
<td>0</td>
<td>650</td>
</tr>
<tr>
<td>Drude term</td>
<td>2550</td>
<td>0</td>
<td>40</td>
</tr>
</tbody>
</table>

Lorentz term was also included at the position of the strongest phonon feature.

While for $\vec{E} \parallel b$ the Drude–Lorentz model produces an overall spectrum similar to that observed, the large phonon feature near 1270 $cm^{-1}$ in the $\vec{E} \parallel c$ spectrum has an asymmetric shape which cannot be reproduced in this type of calculation. The asymmetric shape is a result of interaction between the phonon and the broad electronic background, which are assumed to be completely independent in the Drude–Lorentz model. One of the earliest and most general approaches to account for such interactions is that published by Fano[115]. Most models which have been developed to deal specifically with the organic conductors also include this type of interaction. The results from one such calculation, the phase–phonon model, are presented in the next section.

Phase–phonon Model

The phase–phonon model has frequently been used to simulate the optical spectra of the organic semiconductors with low dimensionality[116, 117]. The starting point for this model is a broad background of a one–dimensional semiconductor, having zero conductivity up to the gap energy and then a singularity followed by $1/\sqrt{\omega}$ energy dependence. This part of the optical response is based on a Hamiltonian which assumes the presence of a charge–density–wave and a periodic distortion of the lattice. Onto this background,
Figure 3.26: The Drude–Lorentz model can produce a spectrum similar to that measured for \((BEDT-TTF)_2[Cu(NCS)_2]\) for \(E \parallel b\). Two Drude terms are required to simulate both the high conductivity in the 200 \(\text{cm}^{-1}\) to 1000 \(\text{cm}^{-1}\) region and the narrow low-frequency conductivity peak.
phonon features are superimposed. As with the Fano-model, the coupling between the broad background and narrow phonon features is included.

The phase-phonon model is unique in the way it allows excitation of molecular vibrations through a mechanism of charge transfer between molecules. The "phase" part of phase-phonon refers to displacements of the charge-density-wave in relation to the nearly stationary periodic distortion of the lattice. This displacement of charge with respect to the lattice produces a dipole moment which couples to optical radiation. Coupling of these charge oscillations to internal molecular-phonon-vibrations takes place through electronic charge being pushed on and off the individual molecules. Through this mechanism, the totally symmetric modes of vibration, which have no dipole moment and which would normally not be seen in the optical spectra, become activated.

For modelling the optical properties of \((BEDT-TTF)_2[Cu(NCS)_2]\), a material with high metallic conductivity in two-dimensions, the phase-phonon model is clearly not the most logical starting point. In particular, the assumption of a one-dimensional semiconducting background is not appropriate. However, by applying a large damping term to this part of the spectrum, it is possible to produce a broad spectrum in reasonable agreement with the measurement. The phase-phonon model then has the ability to deal correctly with the interaction between the phonons and the electronic background.

The model input parameters are listed in Table 3.2 and the resulting spectra are shown in Figure 3.27. The first three parameters, the plasma frequency, \(\omega_p\), the semiconducting gap energy, \(2\Delta\), and the damping, \(\eta\), were used to determine the characteristics of the background one-dimensional semiconducting band[118]. The terms, \(V/\Delta\) and \(\epsilon_c\), are involved in the coupling of the phonon to the background. Characteristics of the one phonon vibration included in this calculation are the fundamental frequency, \(\omega_i\), the width, \(\gamma_i\), the coupling strength, \(\lambda_i\).

Keeping \(\omega_p\) and \(\eta\) fixed, and adjusting only the gap energy, \(\Delta\), it was possible to
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Table 3.2: Parameters for the phase–phonon model which produce a good fit to the measured low temperature \((BEDT-TTF)_{2}[Cu(NCS)_{2}]\) conductivity.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(\vec{E} \parallel b)</th>
<th>(\vec{E} \parallel c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma frequency, (\omega_{p}) (cm(^{-1}))</td>
<td>7250</td>
<td>7250</td>
</tr>
<tr>
<td>Gap parameter, (2\Delta) (cm(^{-1}))</td>
<td>3500</td>
<td>2180</td>
</tr>
<tr>
<td>Damping, (\eta) (cm(^{-1}))</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>(\varepsilon_{c})</td>
<td>3.2</td>
<td>3.5</td>
</tr>
<tr>
<td>(V/\Delta)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Phonon frequency, (\omega_{i}) (cm(^{-1}))</td>
<td>1550</td>
<td>1550</td>
</tr>
<tr>
<td>Phonon damping, (\gamma_{i}) (cm(^{-1}))</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Phonon coupling, (\lambda_{i}) (cm(^{-1}))</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Total coupling, (\lambda)</td>
<td>0.16</td>
<td>0.16</td>
</tr>
</tbody>
</table>

obtain broad spectral characteristics similar to the low temperature measurements for both polarizations. The observed low-frequency conductivity peak is missing but could be added separately. The damping term included in this model produced a spectrum with strong conductivity down to low frequency, a characteristic which is seen in the low temperature data but not at temperatures above 50 K. For the higher temperature measurements, this low frequency part of the spectrum cannot be fit using this model.

In addition to producing the appropriate shape of the phonon part of the \(\vec{E} \parallel c\) spectrum, the position of the feature behaves in an interesting way. Because the vibration is excited through coupling to the broad background, both the shape and the position are affected by the change in the gap energy. Interaction with the background shifts the position down from the fundamental frequency of 1550 cm\(^{-1}\) to 1287 cm\(^{-1}\) for \(\vec{E} \parallel b\) and 1272 cm\(^{-1}\) for \(\vec{E} \parallel c\). For \(\vec{E} \parallel c\), the close proximity of the phonon to the background peak produces a broader phonon which is moved to slightly lower energy than that calculated for \(\vec{E} \parallel b\). Both these characteristics are observed in the measurement. At 12 K, the \(\vec{E} \parallel c\) conductivity spectrum has an asymmetric phonon peak at 1274 cm\(^{-1}\), while the same vibration for \(\vec{E} \parallel b\) is quite narrow and appears at 1338 cm\(^{-1}\). The much higher
Figure 3.27: The phase–phonon model can produce a spectrum similar to that measured for \( (BEDT-TTF)_2[Cu(NCS)_2] \) for both polarizations. A single phonon vibration has been included to produce the dominant phonon peak seen in the measured spectra. The only change between the two spectra is the value of the gap parameter, which locates the mid–infrared peak[110].
position of the phonon in the $E \parallel b$ measured spectra can easily be matched using the phase-phonon model by adjusting the phonon coupling parameter from $\lambda = 0.060$ to $\lambda = 0.045$.

3.2.4 Estimations of $\omega_p$ and Application of Sum Rules

Measurement of the plasma frequency is a common starting point for analysis of the electronic properties of a material. In a conducting medium, the plasma frequency is defined as the resonant frequency for the oscillations of the free electrons against the fixed positive nuclei. In this case, the plasma can also be thought of as the frequency above which conduction electrons can no longer respond fast enough to prevent propagation of an electromagnetic wave. In both the simple free-electron model and the more complicated Drude-Lorentz model, the plasma frequency, $\omega_p$, is a function of the electron density, $n$, and the effective mass, $m^*$:

$$
\omega_p^2 = \frac{4\pi ne^2}{m^*} \quad \text{(cgs)}
$$

$$
\omega_p^2 = \frac{ne^2}{\epsilon_0 m^*} \quad \text{(SI)}.
$$

(3.5)

Four simple methods for estimating a value of $\omega_p$ will be discussed here, and comparisons will be made between the room temperature and low temperature measurements. For reference, the results are summarized in Table 3.3, appearing at the end of this section.

Fitting of the Mid-infrared Reflectance

In the free-electron picture of the Drude model, the optical response of the sample is estimated using Equation 1.27 with the Lorentz-oscillator terms set to zero. The remaining Drude-portion is:

$$
\varepsilon(\nu) = \varepsilon' + i\varepsilon'' = \varepsilon_e - \frac{\omega_p^2}{\omega(\omega + i\gamma)}.
$$

(3.6)
Mid-infrared reflectivities of the organic conductors have a basic shape somewhat similar to that derived from this Drude response, and this formula is often applied to obtain estimates for $\varepsilon_c$, $\omega_p$, and $\gamma$.

Figures 3.28 and 3.29 show that this model can give a good fit to the data at frequencies above about $3500 \text{ cm}^{-1}$. All three parameters, $\varepsilon_c$, $\omega_p$, and $\gamma$ have been obtained using a least squares fitting routine. While the fit is good in this high frequency region, the overall fit is poor, as demonstrated by Figures 3.30 and 3.31. Our low temperature measurements show that the mid-infrared part of the spectrum is influenced by interband transitions, not the conduction electrons, so the derived value of $\omega_p$ is not directly related to the electrons involved in dc conductivity. However, a plasma frequency derived from the mid-infrared fit can still be interpreted as the frequency at which light begins to propagate into the material.

**Zero Crossing of $\varepsilon(\omega)$**

For a simple metal obeying Equation 3.6, an easy way to determine $\omega_p$ is by looking at the real part of $\varepsilon$:

$$\varepsilon'(\omega) = \varepsilon_c - \frac{\omega_p^2}{\omega^2}. \quad (3.7)$$

At a frequency of $\omega = \omega_p/\sqrt{\varepsilon_c}$, the function $\varepsilon'(\omega)$ will pass through zero. Although we have already seen that $(BEDT-TTF)_2[Cu(NCS)_2]$ does not have the optical characteristics of a simple Drude metal, the function $\varepsilon'(\omega)$ does show an interesting dependence on polarization which is related to the relative positions of the peaks in the mid-infrared.

Figure 3.32 shows $\varepsilon'$ for the two polarizations for the $(BEDT-TTF)_2[Cu(NCS)_2]$ sample at 12 K. The general shape is similar to that predicted by Equation 3.7, with $\varepsilon'$ large and negative in the far-infrared, but gradually increasing to cross zero in the mid-infrared region. Zero crossings are at $1945 \text{ cm}^{-1}$ and $4005 \text{ cm}^{-1}$ for $\vec{E} \parallel b$ and $\vec{E} \parallel c$. 
Figure 3.28: Drude-reflectivities can be fit to the measurements in the mid-infrared region. Three parameters are adjusted to obtain the best fit: the plasma frequency, the damping, and the background polarization. Performing the fitting in this frequency region gives these parameters values corresponding to properties of the interband transitions rather than the dc electronic response.
Figure 3.29: Drude-reflectivities fit to the low temperature measurements.

\[ T = 12 \text{ K} \]

\[
\begin{align*}
\text{(BEDT-TTF)}_2 \\
\text{[Cu(NCS)\textsubscript{2}]} & \quad \text{E} \parallel \text{b} \\
\text{E} \parallel \text{c}
\end{align*}
\]

- \( \omega_p = 8730 \text{ cm}^{-1} \)
- \( \gamma = 1260 \text{ cm}^{-1} \)
- \( \epsilon_c = 3.37 \)
- \( \omega_p = 8520 \text{ cm}^{-1} \)
- \( \gamma = 1195 \text{ cm}^{-1} \)
- \( \epsilon_c = 4.13 \)
Figure 3.30: While the Drude fit works well in the mid-infrared, the agreement at lower frequency is not good. The model is based on the frequency dependent response of free electrons, an assumption is not appropriate in this case where the mid-infrared optical response is characteristic of band transitions.
Figure 3.31: Overall view comparing Drude-reflectivities to the measured low temperature reflectivity.
respectively. Using the values of $\epsilon_c$ derived from the reflectivity fit gives values of $\omega_p$ of 3480 cm$^{-1}$ and 7490 cm$^{-1}$.

In comparison with the results of the fit to the reflectivity, the $\vec{E} \parallel c$ zero crossing gives a value of $\omega_p$ in reasonable agreement while that for $\vec{E} \parallel b$ is at a much lower frequency. For $\vec{E} \parallel b$, the interband transitions occur at a relatively high frequency and the zero crossing is at least partially determined by the actual conduction electron response. For $\vec{E} \parallel c$, however, the interband and conduction electron responses are not widely separated, giving the overall spectrum a shape more like the simple Drude picture. Thus, the zero crossing for the $c$ polarization occurs at a higher frequency corresponding to the slightly more Drude-like overall shape of the optical response.

**Analysis of the Loss Function**

Another common method for obtaining a value of the plasma frequency is by rearranging the optical response in terms of the loss function:

\[
\text{Loss Function} = -\text{Im} \left[ \frac{1}{\tilde{\epsilon}(\omega)} \right].
\]  

(3.8)

This parameter is directly proportional to the rate of scattering for fast electrons travelling through the material and, in a normal metal, has a maximum at the energy corresponding to excitation of oscillations at the plasma frequency. For materials with background polarizability, $\epsilon_c$, the peak appears at the frequency:

\[
\Omega_p = \frac{\omega_p}{\sqrt{\epsilon_c}}.
\]

(3.9)

For $(BEDT-TTF)_2[Cu(NCS)_2]$ at room temperature, the loss function shown in Figure 3.33 has strong peaks at 4450 cm$^{-1}$ and 3980 cm$^{-1}$ for the two polarizations. Multiplying by the appropriate factors of $\sqrt{\epsilon_c}$ gives the plasma frequencies of 8420 cm$^{-1}$ and 7770 cm$^{-1}$ for $\vec{E} \parallel b$ and $\vec{E} \parallel c$. Similar curves are shown for the sample at 12 K,
Figure 3.32: In the simple Drude model, the zero crossings of $\epsilon'$ occur at a frequency of $\omega_p/\sqrt{\epsilon_r}$. In this case however, the Drude response is distorted by the presence of interband transitions. For $\vec{E} \parallel b$, these interband transitions are at a much higher frequency and the zero crossing occurs at a position influenced by the shape of the low frequency part of the spectrum. For $\vec{E} \parallel c$, the lower frequency interband transitions give the overall spectrum a more Drude-like shape, and the zero crossing appears at higher frequency.
giving values of 8995 $cm^{-1}$ and 8475 $cm^{-1}$ for the two polarizations. These results are in good agreement with the mid-infrared fit to the reflectivity. It should be noted, however, that the peak in the loss function in these spectra is associated with interband transitions and not the oscillations at the plasma frequency in the normal metals.

**Sum Rules**

There are two sum rules which will be applied to give estimates for $\omega_p [114, 119]$:

\[
I_{\sigma}(\omega) = \left[ \frac{120}{\pi} \int_0^\infty \sigma(\nu) d\nu \right] \overset{\omega \to \infty}{\longrightarrow} \omega_p^2
\]

\[
I_p(\omega) = \left[ -\frac{2\epsilon^2}{\pi} \int_0^\infty \text{Im} \left[ \frac{1}{\epsilon(\nu)} \right] \nu d\nu \right] \overset{\omega \to \infty}{\longrightarrow} \omega_p^2.
\]

With $\sigma(\nu)$ measured in units of $(\Omega cm)^{-1}$, both integrals give a result with units of $cm^{-2}$. Once again, the factor of ($\epsilon^2$) has been included to account for the background polarizability of the sample. In the limit, $\omega \to \infty$, both $I_{\sigma}(\omega)$ and $I_p(\omega)$ should approach $\omega_p^2$. This high frequency limit is the same in both cases, despite the fact that $I_{\sigma}$ is dominated by the low frequency conductivity while $I_p$ is most dependent on the region around $\omega_p/\sqrt{\epsilon}$ where the loss function has a maximum.

The important feature of these sum rules is that most of the interactions which can affect the shape of the spectrum cause no change in the high frequency limit of the integral. Values of $\omega_p$ derived using the sum rules should not be affected either by changes in the electron-phonon interactions, or by the development of an energy gap due to a Peierls distortion. One situation which can affect the integral is a short range interaction preventing two electrons from occupying the same site[119].

The functions $I_{\sigma}(\omega)$ and $I_p(\omega)$ are shown in Figures 3.34 and 3.35. The results from both types of integration are in reasonable agreement at both temperatures. The resulting values of $\omega_p$ are about 6000 $cm^{-1}$ at room temperature and 6500 $cm^{-1}$ to 7500 $cm^{-1}$ at low temperature.
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Figure 3.33: For a metal, the loss function has a peak at a frequency corresponding to the excitation of oscillations at the frequency, $\omega_p/\sqrt{\varepsilon_c}$. In this case however, the loss function peak must be interpreted in terms of excitation of interband transitions.
Figure 3.34: Sum rule integration over the conductivity. The values of the integral at a frequency of 8000 cm⁻¹ are indicated for each curve.
Figure 3.35: Sum rule integration over the loss function, Im[1/ε]. The values of the integral at a frequency of 8000 cm\(^{-1}\) are indicated for each curve.
Comparison of the results from the two sum–rule integrals indicates that the estimated value of \( \epsilon_c \) is reasonably accurate. The sum rule, \( I_\sigma \), has no dependence on the value of \( \epsilon_c \) while \( I_p \) incorporates a factor of \( \epsilon_c^{-2} \) to account for the background polarizability. Agreement between the \( I_\sigma \) and \( I_p \) integrals in the high frequency limit could only be obtained with reasonable estimates for the factors of \( \epsilon_c \).

**Summary of Plasma Frequency Analysis**

Table 3.3 summarizes the results of the various approaches which have been used here to approximate the plasma frequency. There are several trends which can be noted. The highest estimates come from the analysis of the reflectivity fit and the loss function. This is because these methods are dependent only on the particular shape of the optical spectrum in the 3500 cm\(^{-1}\) to to 4500 cm\(^{-1}\) range. This is a region where the optical response changes rapidly due to the band structure properties of the sample, and is only indirectly affected by the metallic nature of the sample. Both the sum rules and the zero crossing of \( \epsilon' \) for \( \vec{E} \parallel b \) are more directly related to the lower frequency part of the spectrum where the low temperature metallic response is important. In these cases, a lower value of the plasma frequency results. A second characteristic evident in Table 3.3 is that the plasma frequency is significantly higher at low temperature than at room temperature. According to Equation 3.5, this could result from either an increase in the number of charge carriers, \( n \), or a decrease in the effective mass, \( m^* \).

Using these estimates of \( \omega_p \) in Equation 3.5 allows derivation of the effective mass of the electrons involved in the optical response. For this organic conductor, the number density of electrons in the conducting plane is 1/2 electron per \( ET \) molecule. With the resulting number density, \( n = 1.23 \times 10^{21} \text{cm}^{-3} \), the effective mass derived from either the mid-infrared reflectivity or the loss function peak is \( m^* \approx 1.5m_e \). The sum rules give \( m^* \approx 2.4m_e \). These results can be compared with the more direct measurements
Table 3.3: Values of $\omega_p$ derived by various types of analysis of the optical spectrum of $(BEDT-TTF)_2[Cu(NCS)_2]$.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Polarization</th>
<th>$\epsilon_c$</th>
<th>$\omega_p(cm^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zero crossing of $\epsilon'$</strong></td>
<td>12 K</td>
<td>$\vec{E} \parallel b$</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>12 K</td>
<td>$\vec{E} \parallel c$</td>
<td>4.13</td>
</tr>
<tr>
<td><strong>R fit</strong></td>
<td>295 K</td>
<td>$\vec{E} \parallel b$</td>
<td>3.43</td>
</tr>
<tr>
<td></td>
<td>295 K</td>
<td>$\vec{E} \parallel c$</td>
<td>3.81</td>
</tr>
<tr>
<td></td>
<td>12 K</td>
<td>$\vec{E} \parallel b$</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>12 K</td>
<td>$\vec{E} \parallel c$</td>
<td>4.13</td>
</tr>
<tr>
<td><strong>Loss function</strong></td>
<td>295 K</td>
<td>$\vec{E} \parallel b$</td>
<td>3.43</td>
</tr>
<tr>
<td></td>
<td>295 K</td>
<td>$\vec{E} \parallel c$</td>
<td>3.81</td>
</tr>
<tr>
<td></td>
<td>12 K</td>
<td>$\vec{E} \parallel b$</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>12 K</td>
<td>$\vec{E} \parallel c$</td>
<td>4.13</td>
</tr>
<tr>
<td><strong>Sum rule</strong></td>
<td>295 K</td>
<td>$\vec{E} \parallel b$</td>
<td>3.43</td>
</tr>
<tr>
<td><strong>$I_s(8000cm^{-1})$</strong></td>
<td>295 K</td>
<td>$\vec{E} \parallel c$</td>
<td>3.81</td>
</tr>
<tr>
<td></td>
<td>12 K</td>
<td>$\vec{E} \parallel b$</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>12 K</td>
<td>$\vec{E} \parallel c$</td>
<td>4.13</td>
</tr>
</tbody>
</table>
of the effective mass of the conduction electrons obtained from the Shubnikov–de Haas measurements, which give $m^* \approx 3.4m_e$. The difference between our result and that of the Shubnikov–de Haas measurements might be due to the fact that the optical measurement gives an average effective mass for all electrons (both those participating in interband and intraband transitions), while the Shubnikov–de Haas result looks specifically at the electrons participating in electrical conduction. Using either technique, a considerable enhancement of the electronic mass is observed.

3.3 Smaller Picture: Vibrational Phonon Features of Protonated and Deuterated Salts

The phonon spectra of traditional superconductors are interesting because of the fundamental connection between superconductivity and low frequency phonons. Our measurements on the $(BEDT-TTF)_2[Cu(NCS)_2]$ organic superconductor show the presence of many molecular phonon vibrations throughout the far and mid-infrared. Assignments of the observed features to the molecular normal modes of vibration show that both normally-active and normally-inactive modes are present in the spectra. As previously mentioned, electronic coupling plays an important role in the excitation of these phonon vibrations.

3.3.1 Normal Modes of Vibration and Group Theory

The normal modes of vibration for an isolated ET molecule have been calculated by Kozlov, Pokhodnia, and Yurchenko, using the methods of normal coordinate analysis[120, 121]. Molecular normal modes are the resonant frequencies at which all masses move in phase, passing through the equilibrium positions simultaneously and reaching positions of maximum displacement simultaneously. For each mode, both the frequency and the
distribution of energy among the molecular bonds were calculated. Input parameters for the calculation were the atomic positions and the force constants between neighbouring atoms, which were defined using the internal coordinate system shown in Figure 3.36. Values of the inter-atomic force constants were refined to give a good fit between the calculated frequencies and the measured infrared and Raman spectra on both protonated and deuterated ET samples.

Because of the complexity of the normal coordinate calculation, the out-of-plane distortion of the outer rings of the ET structure was neglected, making the molecule planar with $D_{2h}$ symmetry [121]. $D_{2h}$ symmetry describes a molecule which looks exactly the same after it is either rotated through 180 degrees about one of the cartesian $x$, $y$, or $z$ axes (with the origin in this case positioned at the centre of the molecule on the $C = C$ bond), reflected through the $xy$, $xz$, or $yz$ planes, or inverted through the origin. The position and orientation of these symmetry axes with respect to the ET molecule are shown in Figure 3.37.

Frequencies and potential energy distributions derived by Kozlov et al. using the normal coordinate analysis for ET molecule are reproduced in Table 3.4. For the 26 atoms in an ET molecule, there are a total of 78 degrees of freedom. Subtracting the 6 rigid translations and rotations leaves 72 internal modes of vibration. These internal vibrations are divided into four types according to their symmetry species. Vibrations in which the atomic motions are symmetric with respect to the 180 degree rotations are labelled $a$, while those which are antisymmetric are labelled $b_1$, $b_2$, or $b_3$, according to the principle axis of the vibration. Within the $a$ and $b$ categories, the vibrations are divided again into those which are symmetric with respect to inversion about the centre of symmetry (labelled $g$ for the german word gerade meaning even) and antisymmetric (labelled $u$ for ungerade). All the $g$ modes and the $a_u$ mode have no dipole moment and thus are not activated in optical spectra (although $b_g$ modes can be observed using Raman
Figure 3.36: Internal coordinates of BEDT – TTF as defined for the analysis of the normal modes of vibration. The numbers on the bonds are the labels used in the normal coordinate analysis, and the numbers on the atoms refer to the charge distribution on the neutral molecule (to the right), and the charge +1 cation (to the left)[121].

spectroscopy), while the $b_u$ modes have a dipole moment and can be directly activated by the infrared radiation. The columns listing the potential energy distributions in Table 3.4 include those bond stretches or bends contributing at least 15% of the total energy of the mode. A single subscript indicates a stretch, while a pair refers to an angle bend.
Figure 3.37: (a) Directions of the molecular symmetry axes. (b) A schematic diagram of the ET molecule with arrows indicating motions associated with the normally active $\nu_{49}(b_{2u})$ mode. (c) An view of the $bc$ plane of the $\kappa$–phase crystal. Because the long molecular axes are perpendicular to this plane, only the $b_{2u}$ and $b_{3u}$ modes would be expected to appear in the optical spectrum[111].
Table 3.4: Calculated frequencies for all the normal modes of vibration for (BEDT-TTF)$_2$[Cu(NCS)$_2$] in both the protonated ($h_8-$) and deuterated ($d_8-$) forms are shown here. Subscripts in the potential energy distribution refer to the specific molecular bonds participating in the vibrations. A single subscript refers to a stretch of the bond, while a pair of numbers refers to an angle bend. All frequencies are in $\text{cm}^{-1}$.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>$h_8, \nu_i$</th>
<th>Potential energy distribution (%)*</th>
<th>$d_8, \nu_i$</th>
<th>Potential energy distribution (%)*</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_g$</td>
<td>1</td>
<td>2949 $K_{22}(98)$</td>
<td>2177 $K_{22}(93)$</td>
<td>-772</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1554 $K_1(59), K_{10}(17)$</td>
<td>1554 $K_1(59), K_{10}(17)$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1489 $K_{10}(62), K_1(17)$</td>
<td>1489 $K_{10}(62), K_1(17)$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1415 $K_{22,23}(75)$</td>
<td>1141 $K_{20}(43), K_{20,22}(16)$</td>
<td>-274</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1256 $K_{16,22}(40)$</td>
<td>999 $K_{22,23}(53), K_{16,22}(26)$</td>
<td>-257</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>983 $K_{20}(51), K_{16}(24)$</td>
<td>794 $K_{16}(30), K_{16,22}(17)$,</td>
<td>-189</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_{20,22}(22)$</td>
<td></td>
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*Only contributions greater than 15% included.
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\*Only contributions greater than 15% included.

\^\Delta–out–of–plane deformation.
Table 3.4: Previous table continued

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*Only contributions greater than 15% included.

†\( \Delta \)–out-of-plane deformation.
The assumption of an \( ET \) molecule with \( D_{2h} \) symmetry has been used as an approximation of the real molecular structure. As mentioned previously, the atoms on the outer rings occupy positions slightly off the plane of the inner \( C_2S_4 \) group. In addition, when the molecule is incorporated into the solid, there will be crystal fields which further distort the shape. Reduction of molecular symmetry due to these effects alters the characteristics of Raman and infrared activity, but has only a small affect on the vibrational frequencies. The external forces on the molecule due to the crystal field are accounted for using the techniques of group theory. In the \( \kappa \)-phase of \((BEDT-TTF)_2[Cu(NCS)_2]\), the \( ET \) molecules occupy sites in the lattice about which there are no allowed symmetry operations. This means that there are no rotations (other than multiples of 360 degrees), reflections, or inversions about these points which bring the lattice back onto itself. This lack of site symmetry removes all the molecular symmetry, with the result that all 72 modes derived assuming \( D_{2h} \) symmetry become both infrared and Raman-active.

The effects of the site symmetry and the unit cell symmetry on the infrared and Raman-activity of the modes of vibration are demonstrated in the correlation table, Table 3.5. The first column lists the 72 infrared and Raman-active internal modes of vibration for the isolated \( ET \) molecule, assumed to have \( D_{2h} \) symmetry. Distortion due to lack of site symmetry is considered in the second column, where all 72 of modes become both infrared and Raman active. In the third column, the effect of the arrangement of four \( ET \) molecules in the unit cell with \( P2_1 \) symmetry is considered. For each mode of vibration for the isolated \( ET \) molecule, there are 4 new modes depending on whether the vibrations of the different molecules are in phase or 180 degrees out of phase. From the \( P2_1 \) symmetry of the unit cell, it is shown that all of these modes are both infrared and Raman active, being divided into those which have dipole moment strictly along the \( b \) axis, and those with a component lying within the \( ac \) plane[122].
Table 3.5: Correlation diagram for \((BEDT-TTF)_2[Cu(NCS)_2]\). R=Raman active; ir=infrared active; ia=inactive.

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Before discussing particular assignments, it is useful to consider the relationship between the orientations of the molecules in the solid and the expected polarization dependence of the vibrational absorption strength. Figure 3.37(a) shows the \(b_1\), \(b_2\), and \(b_3\) axes used in the normal mode analysis in relation to the orientation of the molecule. For a normally active \(b_{2u}\) mode, such as \(\nu_{49}\) shown in Figure 3.37(b), there is a bending of the molecule within the plane which produces a dipole moment along the molecular \(b_2\) axis. Figure 3.37(c) shows the orientation of the molecules within the \(bc\) plane on which our reflectivity measurements were performed. Looking at this plane of the crystal structure, the \(ET\) molecules are seen from the end, and the long axis of the molecule is nearly perpendicular to the surface. This means that only the \(b_{2u}\) and \(b_{3u}\) modes have a dipole moment which will interact strongly with the radiation. Figure 3.37(c) demonstrates that the molecular \(b_2\) and \(b_3\) molecular axes are not aligned with the crystalline \(b\) and \(c\) axes. There is, however, a slight tendency towards an orientation of \(b_2\) parallel to the \(c\) axis, which will lead to a stronger response of the \(b_{2u}\) modes to light polarized with \(\vec{E} \parallel c\).
Conversely, the $b_{3u}$ modes should display greater strength in the $\vec{E} \parallel b$ spectra. Structure measurements show that this polarization dependence should be a small effect since the angle between pairs of ET molecules is very close to 90 degrees. For the two different nearly-orthogonal pairs of ET molecules within the unit cell, the measured angles of separation are 82 and 88 degrees[18].

3.3.2 Assignments of Phonon Vibrations and Effects of Electron–Molecular–Vibrational Coupling

Most of the observable phonon vibrations lie in the frequency region between 400 $cm^{-1}$ and 1300 $cm^{-1}$. Figures 3.38 and 3.39 cover this region for both protonated and deuterated samples at low temperature with light polarized along the $b$ and $c$ axes respectively. Table 3.6 lists the vibrations indicated in these figures, plus a few which appear at higher frequency. Features from the protonated and deuterated spectra have been assigned to the most likely vibrational modes based on comparisons between the observed frequencies, the isotope shifts, and the relative strengths in the $\vec{E} \parallel b$ and $\vec{E} \parallel c$ spectra. In Table 3.6, the frequency and strength of each feature is indicated for both polarizations, along with the isotope shift, $\Delta$. The last three columns give the calculated frequencies and shifts from the work of Kozlov et al[120, 121].
Figure 3.38: The phonon features in the spectrum of $\textit{BEDT-TTF}_2\text{[Cu(NCS)]}_2$ lie mostly in the range below 2000 cm\(^{-1}\). Shown here are the spectra measured at low temperature with the protonated sample (lower curve) and deuterated sample (upper curve) and light polarized along the \(b\) axis.
Figure 3.39: Phonons in the low temperature conductivity spectra for $E \parallel c$. 
Table 3.6: Frequencies and assignments of the vibrational features in the infrared conductivity spectra of protonated and deuterated $(BEDT-TTF)_2[\text{Cu(NCS)}_2]$. Sample temperatures were 12 K and 25 K for the protonated ($h_8-$) and deuterated ($d_8-$) samples respectively. All frequencies are in cm$^{-1}$.

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<td></td>
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<td></td>
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$^a$ Calc. freq. = Calculated frequency
$^b$ Calc. shift = Calculated shift

Note: The frequencies are given in cm$^{-1}$, and the assignments are based on the observed vibrational modes in the infrared spectra.
Table 3.6: Previous table continued

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<td></td>
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<td></td>
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<td>809v v9</td>
<td>807w 744w -63</td>
<td>$\nu_{90}(b_{2u})$</td>
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<td>-83</td>
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<tr>
<td>462m 461m -1</td>
<td>457m 441m -16</td>
<td>$\nu_{9}(a_g)$</td>
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</tr>
<tr>
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<td>430m 433m +3</td>
<td>$\nu_{10}(a_g)$</td>
<td>483</td>
<td>-1</td>
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<td></td>
<td>308(RT) 303(RT) -5</td>
<td>$\nu_{11}(a_g)$</td>
<td>318</td>
<td>-2</td>
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vs – very strong, s – strong, m – medium, w – weak, vw – very weak, vvw – very very weak, * – antiresonance dip. Where features are doublets or quartets, the assignment is listed beside the lowest frequency only.

The region where the largest and most interesting phonon features are seen is between about 1000 cm$^{-1}$ and 1400 cm$^{-1}$, which is shown in detail in Figures 3.40 to 3.43. The first two of these diagrams show the temperature dependence for two polarizations and the deuterated sample, while the second pair show similar measurements for the protonated sample. In this region, the protonated spectrum has several different vibrational modes superimposed, a situation which has often led to misinterpretation of this part of the spectrum. Combining the temperature dependence and isotope shifts which we have measured has made it possible to separate the contributions from the various superimposed phonon vibrations.

Features in the $E \parallel b$ spectra of Figures 3.40 and 3.42 are more easily analysed than those observed for $E \parallel c$. Figure 3.42 shows that for this polarization, the protonated
Chapter 3. Reflectivity Measurements

spectrum has just two main features which are partially overlapping at room temperature. As the temperature is lowered, they separate into a quartet centred at about 1280 cm\(^{-1}\) and a broader absorption at 1346 cm\(^{-1}\). Comparison with the deuterated spectra of Figure 3.40, which are superimposed at room temperature and low temperature, shows that the higher frequency mode is largely unaffected by the isotope substitution. For the lower frequency quartet, however, there is a large isotope shift of ~245 cm\(^{-1}\), which leads to assignment to \(v_5(a_g)\), a mode involving \(C-H\) bond bending. The four-fold splitting is a result of the 4 molecules in the unit cell.

Identification of the broader peak at about 1280 cm\(^{-1}\) in the lowest temperature \(E \parallel b\) spectrum begins with the observation that no infrared active vibration is observed at this frequency in measurements on free ET molecules mixed into KBr pellets. This, along with both the large size and the dramatic increase in frequency below 100 K indicates that electron–molecular–vibrational coupling is inducing the vibration of a normally inactive mode. Estimates of the emv coupling strengths from the group theory analysis, also carried out by Kozlov et al, allow identification of this mode. As reproduced in Table 3.7, these results show that the totally symmetric \(v_3(a_g)\) mode is by far the most strongly coupled to the transfer of electronic charge between molecules\[120\]. Strong emv coupling of the \(v_3\) mode, which is illustrated in Figure 3.44, is related to the large concentration of electronic charge on the central part of the molecule. Figure 3.36 shows the calculated charge distribution within the ET molecule for both the neutral and ionized (charge +1) states. When extra charge is either added or taken away from the molecule, it is mostly accommodated on the four sulphur atoms near the centre of the molecule. Thus, the charge-transfer links directly to the inner \(C-C\) bond length, and in particular induces vibrations of the normally inactive \(v_3\) mode.

While the fundamental frequency of this \(v_3(a_g)\) mode is 1489 cm\(^{-1}\), the emv coupling mechanism can easily place the absorption at the observed frequency. The phase–phonon
Figure 3.40: $\bar{E} \parallel b$ optical conductivity of the deuterated sample at various temperatures. The most notable feature is the strong absorption in the 1300 cm$^{-1}$ region, which is assigned to the totally symmetric vibrational mode, $\nu_3(A_g)$. This mode cannot be directly activated by radiation, and is excited through the mechanism of env coupling.
Figure 3.41: $\vec{E} \parallel c$, $d_8-(BEDT-TTF)_2[Cu(NCS)_2]$ phonon spectrum
Figure 3.42: For $\vec{E} \parallel b$ and the protonated sample, the totally symmetric phonon feature observed in the deuterated spectrum can easily be confused with another nearby vibration. The four closely spaced peaks between 1259 cm$^{-1}$ and 1292 cm$^{-1}$ are also observed in the deuterated spectra, but at a frequency shifted down -245 cm$^{-1}$. This large frequency shift allows the modes to be assigned to the stretching modes of the hydrogen bonds on the ends of the ET molecule. The superimposed dashed lines at room temperature and at 30 K show the corresponding spectrum of the deuterated sample.
Chapter 3. Reflectivity Measurements

Figure 3.43: The $\vec{E} \parallel c$ spectrum for the protonated sample has three different features superimposed. When the narrower features near 1180 cm$^{-1}$ and the quartet around 1280 cm$^{-1}$ are superimposed on the broader absorption, they become antiresonances. Once again, the superimposed deuterated spectra help to clarify contributions from the different vibrations.
Figure 3.44: A few of the totally symmetric vibrational modes of the ET molecule are illustrated here. The $\nu_3$ mode is thought to be responsible for the very large phonon peak in the measured $\textit{(BEDT-TTF)}_2\textit{[Cu(NCS)}_2\textit{]}$ spectrum[120].
Table 3.7: Calculated emv coupling constants, \( g_i \), for the 12 \( a_g \) modes of vibration of the ET molecule[120].

<table>
<thead>
<tr>
<th>( a_g ) Mode</th>
<th>( \hbar, \nu_i ) calc. (cm(^{-1}))</th>
<th>( g_i )</th>
<th>( a_g ) Mode</th>
<th>( \hbar, \nu_i ) calc. (cm(^{-1}))</th>
<th>( g_i )</th>
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model includes this type of mechanism and has no difficulty in moving the position of an absorption by this amount. An indication of the coupling strength in \((BEDT-TTF)_2[Cu(NCS)_2]\) is in the observed temperature dependence of the \( \nu_3 \) peak position. In the deuterated \( \vec{E} \parallel b \) and \( \vec{E} \parallel c \) spectra, shifts of +45 cm\(^{-1}\) and +76 cm\(^{-1}\) occur between room temperature and low temperature. Thus, a total shift of several hundred wavenumbers is not unreasonable.

Spectra measured with \( \vec{E} \parallel c \) are shown in Figures 3.41 and 3.43 for the deuterated and protonated spectra respectively. In the protonated spectrum, it is clear that there are three separate features which are superimposed. Two of the features, the \( \nu_5(a_g) \) quartet of \( C-H \) bending modes centred at about 1280 cm\(^{-1}\) and the broad feature due to \( \nu_3(a_g) \) were seen for \( \vec{E} \parallel b \). As has been discussed already, the size and position of the \( \nu_3 \) mode are greatly affected by the strength of the interaction with the mid-infrared absorption band. For \( \vec{E} \parallel c \), this interaction is increased compared to \( \vec{E} \parallel b \) because the mid-infrared band is much lower in frequency. Stronger coupling gives the feature more strength and moves the position down an extra 100 cm\(^{-1}\), where it interacts with the 1180 cm\(^{-1}\) doublet assigned to \( \nu_{67}(b_{3u}) \).
Using similar comparisons of protonated, deuterated, and temperature dependent measurements, most of the other features in the spectra have been assigned. For example, the medium sized group near 450 cm$^{-1}$ is assigned to normally inactive $\nu_9(a_g)$ and/or $\nu_{10}(a_g)$ vibrations. These two modes have calculated frequencies of 483 cm$^{-1}$ and 508 cm$^{-1}$ respectively and have negligible shift with deuteration. In the frequency region between 350 cm$^{-1}$ and 600 cm$^{-1}$, there are no normally active modes which could be assigned to these features.

Appearing at about 890 cm$^{-1}$ is a large feature which we have assigned to the infrared-active $\nu_{49}(b_{2u})$ mode, which gains strength through the emv coupling mechanism. In some studies, this feature has been assigned to a totally symmetric ET vibration, $\nu_7(a_g)$[70]. According to the normal coordinate calculations, however, this mode would have an isotope shift of $-108$ cm$^{-1}$, contrary to our measurements which show no significant change. Other, much weaker features, have been assigned to $\nu_7(a_g)$ in Table 3.6. The only mode with the correct frequency and no isotope shift is the normally active $\nu_{49}(b_{2u})$ mode illustrated in Figure 3.37. This mode will interact through the emv coupling mechanism because, as with the $\nu_3(a_g)$ mode, most of the motion is associated with the central part of the molecule around which the charge transfer mechanism is concentrated. Excitation of this mode, with the observed extra strength for the $\vec{E} \parallel c$ polarization compared to $\vec{E} \parallel b$, is likely, considering the molecular orientations shown in Figure 3.37(c). In this case, the mechanism will involve charge oscillating between neighbouring molecules with different orientations, rather than between the stacked pairs of molecules. An additional indication of electronic coupling to this mode is the presence of the first overtone near 1780 cm$^{-1}$ which appears in both protonated and deuterated spectra, and which would not be infrared active for the isolated molecule.

There are many other weaker features which also fit into the pattern of calculated $a_g$ and $b_{2u}$ modes. Starting from the highest frequency, the simplest $C-H$ stretching
mode is assigned to a doublet near 2900 \text{cm}^{-1}. In this case, the normally inactive \( \nu_1(a_g) \) mode has been assigned although it could also be one of the normally active \( \nu_{44}(b_{2u}) \) or \( \nu_{66}(b_{3u}) \) vibrations which also involve \( C-H \) bond stretches. Near 2100 \text{cm}^{-1}, there is a doublet which is seen in only this particular ET compound and is due to the \( C-N \) stretches in the \([Cu(NCS)_2]^{-}\) anions. In the \( \bar{E} \parallel b \) spectrum, a pair of features near 1407 \text{cm}^{-1} are assigned to \( \nu_4(a_g) \) assuming they shift to 1114 \text{cm}^{-1} \) in the \( d_8 \) spectrum. Another possible assignment, the normally active \( \nu_{45}(b_{2u}) \) mode, was not chosen because the calculated isotope shift of -345 \text{cm}^{-1} \) is too large. The assignments for the remaining small features between 890 \text{cm}^{-1} \) and 1100 \text{cm}^{-1} \) are more speculative but correlations between the chosen \( a_g \) and \( b_{2u} \) modes and the observed features are fairly convincing.

3.4 Conclusions from Reflectivity Measurements

Our reflectivity measurements covering most of the far and mid-infrared spectral regions are important in showing the distinction between the conduction electron and interband absorption contributions to the optical spectrum. As the sample becomes a better conductor at low temperature, we have observed a dramatic rise in the optical conductivity below 500 \text{cm}^{-1}. Extrapolations to \( \omega = 0 \) show good agreement with dc conductivity measurements. At the lowest sample temperature, the half width of the peak is about 40 \text{cm}^{-1}, showing that the scattering time for conduction electrons in this material is relatively long, and that the sample is close to being in the clean superconducting limit. Interband absorption processes are responsible for the optical response of the sample throughout the mid-infrared part of the spectrum. Temperature dependent lattice contraction and a possible phase transition affect the positions of the broad absorption peaks in this region.

Historically, most comparisons between optical conductivities derived from reflectivity
measurements and dc measurements have not produced good agreement. There have been particular problems in the far-infrared region where diffraction effects can easily distort the measured spectrum. Shown in Figure 3.45 is a measurement on one of the other metallic ET based materials which is in disagreement with our results. In this case, the measured reflectivity actually decreases in the region below 300 cm\(^{-1}\), leading to a conductivity spectrum with a very low dc value and a peak in the 300 cm\(^{-1}\) to 500 cm\(^{-1}\) region. These characteristics are not observed in either our bolometric measurements on the same (BEDT\(-\)TTF)\(_2\)AuI\(_2\) material, or in our direct reflectivity measurements on (BEDT\(-\)TTF)\(_2[Cu(NCS)]_2\).

Another important aspect of our work is the ability to measure both the absorption and reflectivity of the sample simultaneously. Knowledge of both these quantities provides an independent means for determining the the absolute scale for the reflectivity. As far as we are aware, these are the only measurements ever performed in which both the specular reflectivity and the bolometric absorption are determined using the same sample.

By analysing the optical response of the sample in various ways, we have estimated the plasma frequency, \(\omega_p\). In a metallic sample, the plasma frequency is related to both the number density and effective mass of the charge carriers. In the organic conductor, the number of available charge carriers is known, and the value of \(\omega_p\) is used to determine the effective mass. From our results, it is seen that the conduction electrons have an effective mass at least twice that of a free electron.

On a smaller scale, our measurements show many phonon absorption features. Most of these have been assigned to specific modes of vibration predicted by the normal coordinate calculations. Combining temperature dependence, polarization dependence, and isotope shifts makes it possible to avoid the common misinterpretations which come with room temperature measurements on a single type of sample. Vibrational assignments
Figure 3.45: A published far-infrared reflectivity measurement on the organic conductor $(BEDT-TTF)_2AuI_2$[57]. The decrease in the measured reflectivity below $300 \text{ cm}^{-1}$ causes a corresponding decrease in derived the far-infrared conductivity and disagreement with the measured dc conductivity.
show that the strongest features are activated $a_g$ modes, as found in many organic conductors, but that normally-active $b_{2u}$ modes are also coupling with the electrons in this two dimensional compound.

There has been some speculation that the electron-phonon interactions at mid-infrared energies play a direct role in the superconductivity of these compounds[71, 125, 126, 127]. Our measurements show no evidence for this type of mechanism. For phonons directly linked to the superconducting mechanism, the Holstein process would be expected to shift the positions in the spectrum by an energy of $2\Delta$. No such effect was observed in the measurements performed with a sample temperature of 6.3 K. Any influence of the mid-infrared phonons on the superconducting mechanism is very unlikely, both because of the large difference in the energy scale, and because optical measurements on both non-superconducting organic materials show similar phonon features.
4.1 Comparison Between Organics and Other Superconductors

Recent increases in the superconducting transition temperatures of both organics and high-$T_c$ ceramics have brought new interest to research on superconducting materials. Figure 4.1 demonstrates how dramatic the recent advances have been, showing the progression of superconducting transition temperatures as a function of time starting from the year 1900.

The organic superconductor, $(BEDT-TTF)_2[Cu(NCS)_2]$, and the high-$T_c$ ceramics have some important characteristics in common, which also distinguish them from traditional metallic superconductors. The most obvious similarity is two-dimensionality, with both the organic and ceramic superconductors consisting of highly conducting planes separated by insulating layers. Another distinguishing feature is a conduction electron density which is a factor of $10^2$ to $10^3$ lower than that in a conventional metallic superconductor. This characteristic is important because the BCS theory predicts a superconducting transition temperature decreasing exponentially with a decreasing Fermi surface density of states, $D(\varepsilon_F)$, according to the equation[9]:

$$T_c = 1.14 \Theta_D e^{[-1/UD(\varepsilon_F)]},$$

where $\Theta_D$ is the Debye temperature describing typical phonon energies, and $U$ is the attractive interaction between electrons. In a BCS superconductor, a low density of
conduction electrons is associated with a low value of $D(\varepsilon_F)$, and a low transition temperature. In these new superconductors, the very low electron density must in some way be compensated by a mechanism increasing the attractive interaction between electrons. Knowledge of the details of this mechanism may ultimately lead to development of new superconductors with higher transition temperatures.

Kresin and Wolf have compared the layered high-$T_c$ and organic superconducting systems based on the theory of a two-dimensional Fermi-liquid\cite{129, 130}. In this analysis, the relations used to derive the Fermi energy, $\varepsilon_F$, the effective mass, $m^*$, and the Fermi velocity, $v_F$, from experimentally determined characteristics are\cite{129}:

\begin{align}
\varepsilon_F &= \left( \frac{\pi^2 k_b^2}{3} \right) \frac{n}{\gamma}, \quad (4.2) \\
m^* &= \left( \frac{3\hbar^2}{\pi} \right) \frac{d_c \gamma}{k_b^2}, \quad (4.3)
\end{align}

and

\begin{equation}
\frac{v_F}{m^*} = \left( \frac{2\varepsilon_F}{m^*} \right)^{1/2}, \quad (4.4)
\end{equation}
Chapter 4. Conclusions

Table 4.1: Comparison of electronic properties of conventional lead, high-\textit{T}_c, and organic superconductors. For the organic and high-\textit{T}_c materials, the two-dimensional Fermi-liquid approach has been used to derive the Fermi energy and velocity.

<table>
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<th>High-\textit{T}_c</th>
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<td>c1.23 \times 10^{21}</td>
<td>d2 \times 10^{21}</td>
</tr>
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<td>d25</td>
<td>f8.8</td>
</tr>
<tr>
<td>(m^*/m_e)</td>
<td>a2</td>
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<td>f5</td>
</tr>
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<td>(\xi_0(\text{Å}))</td>
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<td>g180</td>
<td></td>
</tr>
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<td>(\lambda(\text{Å}))</td>
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<td></td>
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<tr>
<td>(v_f(\text{cm/sec}))</td>
<td>b1.83 \times 10^{8}</td>
<td>j0.4 \times 10^7</td>
<td>k0.1</td>
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<tr>
<td>(\varepsilon_f(\text{eV}))</td>
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<td>k0.07</td>
<td>.1</td>
</tr>
<tr>
<td>(\Delta/\varepsilon_f)</td>
<td>3 \times 10^{-4}</td>
<td>.05</td>
<td>.1</td>
</tr>
</tbody>
</table>

where \(n\) is the density of available electrons in the highly conducting planes, \(\gamma\) is the coefficient for the electronic contribution to the specific heat, and \(d_c\) is the distance separating the highly conducting planes in the material. For example, using the measured values of \(d_c\) and \(\gamma\) in the case of \((\text{BEDT-TTF})_2[\text{Cu(NCS)}_2]\) gives an effective mass of \(m^* = 2.5m_e\), which is in reasonable agreement with the value of 3.5\(m_e\) obtained directly in the Shubnikov-de Haas experiment.

A comparison of the electronic properties of a conventional metal (lead), \((\text{BEDT-TTF})_2[\text{Cu(NCS)}_2]\), and the high-\textit{T}_c materials is made in Table 4.1. Kresin and Wolf suggest that a very important similarity between the high-\textit{T}_c and organic superconductors is the relatively low Fermi energy. The ratio, \(\Delta/\varepsilon_f\), gives an indication of the fraction...
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of the total number of electrons at the Fermi surface which actually participate in the superconducting state. In the conventional metals, this ratio is approximately $10^{-4}$, while assuming a weak coupling BCS gap gives a value $10^2$ to $10^3$ times higher for both the organic and ceramic superconductors. This means that in these new materials, almost all of the conduction electrons at the Fermi surface are paired.

Optical measurements in the infrared are another area of similarity between the organics and other types of superconductors. Figures 4.2 and 4.3 show the reflectivity and conductivity spectra for ceramic and heavy-Fermion superconductors measured at temperatures near $T_c$. These figures show that for both these materials, the normal state conductivity spectra have a Drude-like rise in the low frequency region. This low frequency peak rises in conjunction with the increasing dc conductivity at low temperature, while the higher frequency region is filled in by a broad absorption band with very little temperature dependence. This type of overall spectrum is similar to that observed in our low temperature measurements on \((BEDT-TTF)_2[Cu(NCS)_2]\), as shown in Figures 3.23 and 3.24.

4.2 Organic Superconductivity

Although the mechanism behind the superconductivity in the organic materials is still unknown, it is now believed that \((BEDT-TTF)_2[Cu(NCS)_2]\) is a superconductor in the clean limit, with normal coupling strength, and an anisotropic gap. The best evidence for a clean limit comes from the Shubnikov-de Haas measurements, from which the scattering rate for the normal state conduction electrons can be obtained\[108\]. These results give a Drude term in the optical conductivity with a width of about $3 \text{ cm}^{-1}$, clearly much narrower than the BCS pairing energy, $2\Delta = 25 \text{ cm}^{-1}$, and indicate that the sample is in the clean limit.
Figure 4.2: Reflectivity and conductivity spectra for $YBa_2Cu_3O_{7-\delta}$ have been measured for samples with several different critical temperatures. In each case, the reflectivity is measured for a range of temperatures going through the superconducting transition. The normal state conductivity spectra are similar to those measured for $(BEDT-TTF)_2-[Cu(NCS)_2]$, with a Drude-like conductivity peak at low frequency and other processes contributing absorptance throughout the mid-infrared region.[133].
Figure 4.3: Far-infrared reflectivities and conductivities for the heavy fermion superconductor, $URu_2Si_2$, are similar to those observed for both $(BEDT-TTF)_2[Cu(NCS)_2]$ and the ceramic superconductors[134].
An estimate of the superconducting gap energy has been made using the most recent measurements of specific heat. The jump in the specific heat on entering the superconducting phase is in agreement with the weak coupling BCS prediction, although the width of the transition region introduces some uncertainty to this conclusion[51, 135].

Anisotropy of the energy gap as a function of position on the Fermi surface has been demonstrated by the measurements of magnetic penetration depth as a function of temperature. For an isotropic BCS gap, an exponential temperature dependence would be expected, while the measurements behave as $T^2$. This type of temperature dependence is possible for a gap which is both anisotropic and has nodes at which $\Delta = 0$ at points on the Fermi surface[39].

The objective of our bolometric absorption measurements was to determine the magnitude of the energy gap, $\Delta$. Superconducting electrons should show the characteristic of zero absorption for optical energies below that required to break apart the superconducting pair. In our measurements comparing absorption at various temperatures, no effect due to the superconducting transition is observed. In particular, there is no significant drop in absorption in the region of the optical spectrum below the predicted BCS gap energy. If the superconducting electrons in $(BEDT-TTF)_2[Cu(NCS)_2]$ do condense into a state with zero optical absorptance below the BCS gap energy, $2\Delta$, our measurements show that this part of the optical response is overwhelmed by other absorption processes. Because no effect was observed, neither the questions of the electronic coupling strength, nor of an anisotropic energy gap could be addressed by the optical absorption measurements.

The absence of a superconducting gap in the optical absorption spectrum might be explained by either the clean limit for the superconducting state or by anisotropy of the energy gap. For a clean limit superconductor entering the superconducting state, the electron contribution to the optical conductivity at the gap energy drops to zero from
a value which is already very small, having very little impact on the observable optical properties. The 3 cm\(^{-1}\) wide Drude peak of the Shubnikov–de Haas results would place the bulk of the effect below the range of our measurements. Another indication that the effect of the superconducting transition might be difficult to observe comes from recent measurements at a frequency in the microwave region, showing significant sample absorption at temperatures below \(T_c\)[109]. Extrapolating this microwave result to higher frequencies indicates that at the BCS gap energy, the difference between the normal and superconducting state absorption will be very small. Anisotropy of the energy gap could also play a role in the negative result of our bolometric absorption measurement. If the polarized light is most sensitive to an area around the minimum gap energy, then the presence of an anisotropic gap with nodes at points on the Fermi surface will move the effect of the transition below the spectral range of our measurements.

Our reflectivity measurements give an overall picture of the optical response of the sample. In the mid–infrared there are broad absorption bands, attributed to inter–band transitions, which are relatively temperature independent. The conduction electrons, which are responsible for the metallic characteristics at temperatures below 90 K, contribute to a conductivity peak in the region below 400 cm\(^{-1}\). This peak rises with decreasing temperature, in agreement with measurements of dc conductivity. At a temperature of 12 K, our results show the peak to have a half width of 40±15 cm\(^{-1}\). Although this is much wider than that observed in the Shubnikov–de Haas experiment, it should be emphasized that their measurements were conducted at much lower temperature, and that our result is sensitive to the particular low frequency extrapolation used in the Kramers–Kronig analysis of the reflectivity.

The possibilities for developing new organic superconductors with higher transition temperatures appear to be very good, especially considering the similarities with the
ceramic materials. Further work is certainly needed to explain the nature of these two-
dimensional systems, and to determine the important characteristics involved in pro-
ducing the superconducting state. It is very likely that a better understanding of the
superconducting interaction in these systems with low dimensionality will play a role in
the development of new superconductors for practical applications.
Bibliography


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[54] The spectrometer, model IFS 113V, is made in Germany by Bruker Spectrospin Company. The Canadian distribution and support center is in Milton, Ontario.


[94] Infrared Laboratories, Inc., Tuscon, Arizona, U.S.A.


[96] Diavac "N" pressure gauge, Leybold–Heraeus, Federal Republic of Germany. This type of pressure gauge has a sensitivity which is particularly suited to measuring the pressure above pumped $^4$He. The scale is relatively compressed in the high pressure region where the temperature change is slow, and then expands at lower pressures where the temperature changes more rapidly.

Bibliography


[122] Frances E. Bates, personal communication. See also the character table for a system with $C_2$ symmetry (which is equivalent to $D_{2h}$) as shown in *“Molecular Vibrations,
Bibliography


