ANOMALOUS ABSORPTION

IN

GRANULAR SUPERCONDUCTORS

DISSERTATION

Presented in Partial Fulfillment of the Requirements
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By

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* * * * *

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PUBLICATIONS


PRESENTATIONS


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CHAPTER I

INTRODUCTION

This work deals with a study of the far infrared properties of systems made up of small grains of superconductor. In one case, the grains were isolated spheres imbedded randomly in an insulating, 3-dimensional host. In the other, they were more or less randomly shaped grains in the form of a thin film on an insulating substrate, separated by cracks and voids.

Much effort is being made to understand such materials since they serve as model systems for the study of inhomogeneous media. The electronic properties are especially interesting because of the extreme difference between the electronic properties of the metal inclusions and host. Depending on the concentration of metal, the sample shows either metallic or insulating behavior. This change is observable in the infrared properties of the system. The infrared properties are also affected by the small size and shape of the inclusions.
The first such measurements on mixtures of metal and insulator were performed by Harris\textsuperscript{1}. Later measurements by Tanner, Sievers and Buhrman\textsuperscript{2} revealed an absorption in the far infrared which was many orders of magnitude larger than predicted by theory. More recent measurements have studied the dependence on metal concentration, grain size, and oxide coatings on the grains\textsuperscript{3-5}.

Theoretical work on the subject was first done by J.C. Maxwell Garnett\textsuperscript{6} who used the Clausius-Mossotti relation\textsuperscript{7} to calculate optical properties. Other work using a classical approach was done by Bruggeman\textsuperscript{8}. A quantum mechanical approach was used by Gor'kov and Eliashberg\textsuperscript{9} which treated the effects of the small grain size on the electronic states. Recent theoretical work has been concerned with effects due to eddy currents\textsuperscript{10}, oxide coatings\textsuperscript{11,12}, surface excitations\textsuperscript{13} and other non-local effects\textsuperscript{14}.

The far infrared properties of superconductors are dominated by the appearance of an energy gap in the excitation spectrum\textsuperscript{15}. Measurements of the infrared absorption by superconducting films were first performed by Clover and Tinkham\textsuperscript{16}, followed by the more detailed work of Norman\textsuperscript{17}. Theoretical calculations for the optical response were first done by Mattis and Bardeen\textsuperscript{18}.
More detailed calculations have been done by Prange\textsuperscript{19}. All this work dealt with systems in which inhomogeneities could be ignored. Some infrared measurements on granular superconductors have been done\textsuperscript{2}, but no effect due to superconductivity was noticed. This may have been due to the extremely small grain size in the samples. Other properties of inhomogeneous superconductors have been studied, including work on granular superconductor systems\textsuperscript{20}. Still, the phenomenon of superconductivity in these systems is still not clearly understood.

The organization of this thesis is as follows. Chapter II will discuss the theories for the infrared absorption in granular composites and superconductors. Chapter III explains the procedures for making the samples and lists their characteristics. Chapter IV discusses the far infrared and low temperature experimental technique. Chapter V is devoted to the analysis of the data. Here, the results of the measurements will be presented, showing data which is in strong disagreement with the theoretical predictions. A discussion of these results is presented in chapter VI.
CHAPTER II

THEORY

Introduction

The far infrared absorption of small metal particle composites has normally been treated using self-consistent average field theories. The approximation of average fields should be valid if the size of any inhomogeneity is much smaller than any length scale over which the fields can vary. These length scales are typically the wavelength (so that scattering can be neglected) and the penetration depth (i.e. the skin depth of the metal). The spectral region of interest is for far infrared frequencies (ω<100 cm⁻¹ or λ<100 μm) while the inclusions are small metal particles (radius<1000 Å) imbedded in insulator so that the length scale criteria are reasonably well met.

Average field theories

The most common of these theories are those due to J.C. Maxwell Garnett and D.A.G. Bruggeman. These theories express the average response of an inhomogeneous
material in terms of the response of the individual constituents. The theory due to Maxwell Garnett (MGT) is an unsymmetrical molecular field model that gives for the average dielectric function,

$$\varepsilon_{\text{MGT}} = \frac{\varepsilon_i [(2f+1)\varepsilon_m + (2-2f)\varepsilon_i]}{(2+f)\varepsilon_i + (1-f)\varepsilon_m}. \quad (1)$$

Here, $f$ is the volume fraction for the metallic constituent, and $\varepsilon_i$ and $\varepsilon_m$ are respectively the dielectric functions for the insulator and metal. In this model one material is considered the "host" while the other is the "inclusion".

The theory due to Bruggeman is similar but treats both materials as inclusions in an "effective medium" which is why this symmetric theory is known as the effective medium approximation (EMA). It yields a quadratic equation for the average dielectric function,

$$1(3f+1)\varepsilon_m + (2-3f)\varepsilon_i \varepsilon_{\text{EMA}} - 2(\varepsilon_{\text{EMA}})^2 + \varepsilon_m \varepsilon_i = 0. \quad (2)$$

For metal-insulator composites, the EMA predicts a percolation transition at a critical volume fraction, $f_c = 1/3$. Both these theories assume spherical inclusions which are non-interacting (except through their contribution to the average field).
Stroud has pointed out that small metal particle composites can interact with the magnetic part of an incident field. The shape and size of the grains is such that eddy currents can be induced. This effect can be incorporated in the theory by considering the magnetic polarizability of a particle. For spherical particles we use,

\[ \gamma_{sp} = \left( -\frac{3}{8\pi} \right) \left[ 1 - \frac{3}{ak} + \frac{3\cot(ak)}{ak} \right]. \quad (3) \]

Here, \( a \) is the particle radius and \( k \) is the propagation constant for the wave in the metal. This polarizability is then related to the particle's permeability by

\[ \mu_{sp} = \frac{1 + (8\pi/3)\gamma_{sp}}{1 - (4\pi/3)\gamma_{sp}}. \quad (4) \]

From this expression, the effective permeability of the composite can be determined in a way completely analogous to the calculation for the dielectric function. The resulting expressions are identical in form, i.e. for the MGT,

\[ \mu_{MGT} = \frac{(2f+1)\mu_{sp} + (2-2f)}{(2+2f) + (1-f)\mu_{sp}}. \quad (5) \]
Note that the permeability of the insulator has been taken as unity.

The dielectric response for the metallic constituent has been treated both classically and quantum mechanically. The classical approach uses a Drude model. Because of the small size of the grains, the scattering is dominated by collisions with the surface. For this reason one typically chooses the scattering time to be the time it takes an electron, traveling at the Fermi velocity, to traverse the grain. The form for $\varepsilon_m$ is,

$$\varepsilon_m = 1 - (\omega_p^2/\omega^2 + i\omega/\tau)$$

(6)

where $\tau$ is the scattering time and $\omega_p$ is the plasma frequency.

Quantum mechanical theories

The standard quantum mechanical treatment is that of Gor'kov and Eliashberg. The small size of a metal particle implies that the number of electrons on a single grain is not large. The electron states, which for a bulk metal are a continuum, are now discrete, a phenomenon known as size quantization. Gor'kov and Eliashberg used a statistical approach to determine the density of energy levels within a particular energy
range. With this energy-level distribution and calculations of the associated transition matrix elements, expressions for the dielectric function and magnetic permeability could be obtained. Their results showed that quantum size effects should be observable in the far infrared for metallic grains whose size was less than 50 Å.

The choice of which theory is best depends on the details of the particular system and frequency range being studied. In this study, the grain size is typically 500 Å so that quantum size effects should not be too important. Composites with f above a few percent are essentially opaque in the far infrared which limits transmission studies to composites of low metallic concentration. In the limit of small f, the MGT and ENA theories yield the same results. Therefore, in this thesis, use will be made of the simpler MGT and a classical approach except where superconductivity is involved in which case a quantum mechanical approach is necessary. In both cases, the discreteness of the energy levels will be neglected.

Results and discussion - normal metals

For the composites, the experimentally measured quantity is the absorption coefficient. This is related
to the the response functions through,

\[ \alpha = \frac{2\omega}{c} \text{Im} \left[ \sqrt{\varepsilon(\omega)} \mu(\omega) \right] \]  

(7)

where c is the speed of light. In the limit of small \( f \) and low frequency, the absorption has been shown to be of the form \(^4\),

\[ \alpha(\omega) = \frac{f \omega^2}{c} \left[ (9c/\omega_p^2 \tau) + (a^2 \omega_p^2 \tau / 10c) \right] . \]  

(8)

The first term accounts for electric dipole absorption while the second is that due to eddy currents (magnetic dipole). In this work, the particle radii were 50 Å or larger so that the second term should be the dominant one. In this regime, the absorption coefficient can be expressed in the form,

\[ \alpha(\omega) = Kf \omega^2 \]  

(9)

where \( K \) is proportional to \( a^2 \). Figure 1 shows the absorption coefficient for a composite of small Al particles in KCl as predicted by the MGT. Figure 2 shows the experimentally measured absorption for such a composite \(^5\). The experimental data shows the predicted \( \omega^2 \) dependence but there is a considerable discrepancy in the magnitude of the absorption. This anomalously large
Figure 1. Absorption coefficient for three Al in KCl composites as predicted by the MGT.
Figure 2. Experimentally measured absorption coeff. for pure KCl and three Al in KCl composites.
Plate I. Scanning electron micrograph (top) and X-ray map for Al (bottom) of the surface of an Al in KCl composite.
absorption has been observed by numerous workers\textsuperscript{3-5} and many explanations have been proposed. These theories have dealt with clustering\textsuperscript{22} and surface effects\textsuperscript{12-14}. For the Al data of figure 2, X-ray emission studies of the surface revealed fairly uniform metal particle distributions, suggesting that cluster effects should not be too important. The surface effects include absorption in the oxide coating surrounding each particle\textsuperscript{11,12} and absorption due to the creation of surface phonons\textsuperscript{12}. However, the surface phonon theory gives the wrong dependence on particle size (1/a) and measurements on alumina\textsuperscript{5} show no significant absorption in this oxide as is required by the other theory. One interesting feature of the Al composites is the dependence of the absorption on the volume fraction, f. Whereas in most composites the dependence of a on f is linear\textsuperscript{3,4}, in aluminum the data is closer to $f^2$ (5). This suggests that inter-particle effects (e.g. tunneling) can be important.

Superconductivity - bulk properties and the far infrared

The electromagnetic response of a substance can also be characterized by the complex conductivity for the substance. Expressions for the frequency dependent complex conductivity of a superconductor were first
calculated by Mattis and Bardeen\textsuperscript{18}. Their expressions for the complex conductivity, in terms of the normal state conductivity, were shown to be valid for the case of extremely dirty superconductors. These expressions are

\[ \sigma_{\text{super}} = \sigma_{1s} + \sigma_{2s} \]

\[ \sigma_{1s} / \sigma_n = (1/\hbar \omega) \int_{-\Delta}^{\Delta} \left[ E / (E^2 - \Delta^2)^{1/2} \right] \left[ (E + i\hbar \omega) / [ (E + i\hbar \omega)^2 - \Delta^2 ]^{1/2} \right] \]

\[ \times \left( 1 + \Delta^2 / [ E(E + i\hbar \omega) ] \right) dE , \quad (10) \]

\[ \sigma_{2s} / \sigma_n = (1/\hbar \omega) \int_{-\Delta}^{\Delta} \left[ E / (E^2 - \Delta^2)^{1/2} \right] \left[ (E + i\hbar \omega) / [ (E + i\hbar \omega)^2 - \Delta^2 ]^{1/2} \right] \]

\[ -\Delta \ (\hbar \omega > 2\Delta) \]

\[ \times \left( 1 + \Delta^2 / [ E(E + i\hbar \omega) ] \right) dE , \quad (11) \]

where \( \sigma_n \) is the normal state conductivity and \( \Delta \) is the energy gap for the particular superconductor. Note that the lower limit in eq. (11) differs depending on whether \( \hbar \omega > 2\Delta \). From these expressions one can see that a superconductors response differs from that of a normal metal for two reasons. The first two factors inside the integral are the joint density of states, which for a superconductor has an energy gap and a square root singularity at the edge. The second factor arises from the coherence of the superconducting state. The form of this factor depends on the interaction causing the
Figure 3. Real (dissipative) part of superconductor conductivity ratio for Sn ($\omega = 9.28 \text{ cm}^{-1}$) for type II coherence and no coherence factors.
Figure 4. Imaginary part of superconductor conductivity ratio for Sn ($\omega = 9.28 \text{ cm}^{-1}$) for type II and for no coherence factors.
response. The interaction of a transverse electromagnetic wave with an electron is of the form $\mathbf{p} \cdot \mathbf{A}$, which changes sign under time reversal (type II). If the interaction remained the same under time reversal (type I), then the coherence factor would be,

$$\frac{1-\delta^2}{[E(E+i\omega)\}}.$$  \hspace{1cm} (12)

Figures 3+4 show the real and imaginary parts of the frequency dependent conductivity, as determined from these expressions, for both cases of coherence factors and for the case of no coherence factors, a situation which applies for tunneling between separate superconductors between which there is no phase correlation. Both real and imaginary parts are shown. The real part governs the absorption, and for frequencies above the gap, dominates the reflectance. The imaginary part represents the inductive response of the superfluid component of the superconductor and dominates the reflectance at low frequencies; it contributes nothing to the absorption.

Far infrared transmission and absorption measurements on superconducting films$^{16,17}$ have shown good agreement with the expressions appropriate for an electromagnetic interaction, i.e. type II coherence factors. These samples were, in general, reasonably
uniform and metallic in nature.

Superconductivity and granular systems

The question which now arises concerns how to treat the case of a granular system. Two major features must be considered. First is the effect caused by the possible (or likely) loss of long range order. The order parameter for a superconductor has both a magnitude and a phase. For the case of two superconductors separated by a narrow insulating strip, the state of minimum energy corresponds to a phase difference of zero. This phase alignment is accomplished by Josephson pair tunneling across the insulator. If the insulator is thick, then the tunneling probability becomes zero and phase alignment (long range order) can not occur. When considering the electromagnetic response due to the generation of currents between grains (photon assisted tunneling) one would then expect the case of no coherence factors, discussed above, to apply.

The other feature to be considered is the smallness of the grains themselves. The length scale of importance here is the superconducting coherence length. This length corresponds to the size of a Cooper pair and determines the distance over which the order parameter can vary without an appreciable increase in the
superconductor's energy. As the size of a superconducting grain becomes smaller, the superconducting state becomes less energetically favorable. For grains whose size is comparable to the coherence length, the dominant effect is predicted to be a gap in the density of states whose edge no longer shows the strong singularity of a bulk superconductor$^{23}$. As the grain size becomes less than the coherence length, the energy gap becomes even less pronounced and a true gap can only be found at lower temperatures. In this investigation, the grains were typically of the same size as the coherence length, suggesting that an energy gap should exist on each grain, but it should not have the abrupt features (i.e., square root singularity at the gap edge) of a bulk superconductor. However, there should still be an increase in the density of states at the gap edge.

At present, there are no theoretical calculations which treat the infrared response of a granular superconductor. However, a qualitative prediction can be made incorporating the effects discussed above. The effect of small grain size will have a smoothing effect on $\sigma(\omega)$ near the gap due to the change in the density of states at the gap. Next, if the infrared response is dominated by single grain processes, the coherence
factors should be the same as for the bulk response (type II). The coherence would also be type II for infrared processes between two strongly Josephson coupled grains. As mentioned earlier, infrared response from interactions between uncoupled grains should involve no coherence.

Figure 5 shows the predicted absorption, as calculated using the Maxwell Garnett theory, for a composite of Sn in KCl. Shown are both the normal state absorption and two cases of superconducting absorption. The two cases, type II coherence factors and no coherence factors, should represent limiting values for the superconducting absorption. In either case, for frequencies below the gap, the superconducting absorption should be zero (or non-zero but still small near the gap due to the small grain size effect). For frequencies above the gap, the absorption should approach that of the normal state.
Figure 5. Computed absorption coefficient for a composite of Sn in KCl using the MGT. Normal state and two cases for the superconductive state are shown.
CHAPTER III

SAMPLE PREPARATION

Composites

The composites studied consisted of small metal particles imbedded randomly in a KCl host. The metals used were Sn, Pb and Nb. The Sn and Pb metal particles were produced by the method of noble gas evaporation. The procedure was as follows. An alumina coated molybdenum boat was placed in an evaporator which was then evacuated. Surface impurities were removed by electrical heating. After the boat had cooled, the bell jar was opened to atmosphere and about 0.5 gm of the desired metal was placed in the boat. A clean glass cylinder (diameter=6") was placed around the boat to collect the evaporated metal. After evacuating the bell jar to less than 1x10^-5 Torr, the pumping speed was throttled back by means of a valve. A mixture of argon or helium (75%) and oxygen (25%) was then introduced through a needle valve and flow meter. The oxygen was included to form an oxide coating on the metal particles as they were produced and

(22)
Figure 6. Noble (inert) gas evaporation apparatus.
served to prevent cold-welding between particles as well as to provide electrical isolation. The flow meter was used to ensure that enough oxygen was available during the evaporation to produce a coating of sufficient thickness. By adjusting the pumping speed and gas inlet rate, a constant pressure in the range of 0.1 to 2 Torr could be maintained in the bell jar. The size of the grains produced depended on the type and pressure of the gas present in the bell jar during the evaporation. The higher pressures along with argon gas produced larger grains while lower pressures and helium produced the smallest grains. The metal was now evaporated over a period of 90 seconds during which time an electron microscope stub was momentarily lowered into the metal cloud to collect some of the smoke for later analysis. The metal vapor cloud from the source loses energy to the noble gas atoms causing it to cool and coalesce into small, nearly spherical particles. These particles then collected on the walls of the glass cylinder as a very black "smoke". The evaporation was usually limited to 90 seconds for Sn and Pb smokes because of their low melting points and would melt on the glass cylinder if the evaporation times were too long. After a waiting period to allow cooling, the bell jar was vented with dry nitrogen and the glass cylinder was removed. The smoke
was then collected and stored in a dessicator. The lead smoke required special consideration due to its toxicity and was handled using proper precautions (i.e. filter masks, glove box). Table 1 describes each of the metal smokes produced. Some of the Sn smokes were not truly black, but more of a brown in color, as shown in column 2. Brown smokes were more likely produced when then gas pressures and gas flow rates were high, suggesting that the brown color was due to a thicker oxide coat on the grain surfaces. These smokes were also typically less conducting. Sn batch 5 was melted to the sides of the glass cylinder rendering it useable.

The above method was inappropriate for Nb due to its high melting point. Instead, powder was obtained by collecting filings from a pure Nb rod. These were then sifted to remove particles above 50 micron size. Next, the powder was ground even more finely using a liquid nitrogen immersed mill. The powder was then sifted further resulting in particles with a mean diameter of 8 microns.

Powdered KCL was produced by grinding whole crystals in the mill, under liquid nitrogen. Starting with whole crystals assured both purity and an initially low moisture content, the latter being especially important since KCl is hygroscopic. The resulting typical grain size was several microns.
Table 1. Metal smoke parameters

<table>
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<tr>
<th>Batch</th>
<th>Smoke color</th>
<th>Duration (sec)</th>
<th>Press. (mTorr)</th>
<th>Gas</th>
<th>Flow rate (atm-cc/min)</th>
<th>Radius (Å)</th>
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<tr>
<td>Sn 2</td>
<td>black</td>
<td>45</td>
<td>500</td>
<td>Ar+O</td>
<td>---</td>
<td>200</td>
</tr>
<tr>
<td>Sn 3</td>
<td>brown</td>
<td>50</td>
<td>900</td>
<td>Ar+O</td>
<td>5.0</td>
<td>250</td>
</tr>
<tr>
<td>Sn 4</td>
<td>brown</td>
<td>90</td>
<td>800</td>
<td>Ar+O</td>
<td>5.0</td>
<td>250</td>
</tr>
<tr>
<td>Sn 5</td>
<td>many</td>
<td>120</td>
<td>950</td>
<td>Ar+O</td>
<td>---</td>
<td></td>
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<tr>
<td>Sn 6</td>
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<td>1000</td>
<td>Ar+O</td>
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<td>300</td>
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<tr>
<td>Sn 7</td>
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<td>90</td>
<td>1150</td>
<td>Ar+O</td>
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<td>300</td>
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<td>Sn 8</td>
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<td>1000</td>
<td>Ar+O</td>
<td>4.0</td>
<td>300</td>
</tr>
<tr>
<td>Sn 9</td>
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<td>90</td>
<td>1000</td>
<td>Ar+O</td>
<td>4.0</td>
<td>300</td>
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<tr>
<td>Sn 10</td>
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<td>150</td>
<td>300</td>
<td>He+O</td>
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<td>50</td>
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<td>100</td>
<td>550</td>
<td>Ar+O</td>
<td>2.0</td>
<td>150</td>
</tr>
<tr>
<td>Pb</td>
<td>black</td>
<td>90</td>
<td>500</td>
<td>Ar</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>
Predetermined volumes of both constituents were weighed out and mixed together. The powder was next placed in a die between two pistons. This assembly was put inside an evacuable chamber and pumped to under 1 milliTorr. The powder was compressed, causing the KCl to flow (~10 kbar). The die was then removed, disassembled and the resulting wafer extracted. This wafer was reground and repressed from 3 to 5 times to help achieve uniformity. After the final pressing, the sample was stored in a dessicator to prevent the absorption of water. With this method, 5/8" diameter wafers were produced with thicknesses ranging from 0.5mm to 7mm. Wafers outside these limits were either too fragile or impossible to remove from the die.

Characterization - composites

The first step to characterizing the composites was to determine the mean particle size and distribution. This was accomplished using electron microscopy. A scanning electron microscope (SEM) was used for those samples for which a microscope stub was present in the bell jar during the particular evaporation. All other samples were measured using a transmission electron microscope (TEM). The sample holders consisted of small discs of very fine coated copper screen. A small amount
of the collected smoke was mixed with methyl alcohol in a small vial. This vial was subjected to ultrasonic sound, which served to break up large clumps of the particles and suspend them in the alcohol. A drop of this suspension was then placed on the microscope grid and the alcohol was allowed to evaporate.

For both SEM and TEM the microscope images were recorded on film which allowed for measuring the size of roughly 50 particles for each batch of metal smoke produced.

SEM measurements were also done on a few composites, though this was a rather difficult task due to their non-conductive nature (the SEM relies on a conducting sample to prevent build up of negative charge from the electron beam). The pictures showed nearly featureless surfaces even along fractured surfaces. X-ray mapping for the particular metal in the composite produced uniform patterns suggesting that the grains are randomly distributed. Such an X-ray mapping for an Al in KCl composite is shown in plate I. Mappings for the composites of Sn in KCl were impossible because the characteristic X-rays of tin nearly overlap those of potassium. This uniform distribution of grains is an important characteristic of the samples because the theoretical models assume a random two-component mixture.
Plate II. Scanning electron micrograph (top) and transmission electron micrograph (bottom) of small particle batch Sn 2. Mean radius is 200 Å.
Plate III. Transmission electron micrographs for small particle batches Sn 3 (top) and Sn 4 (bottom) mean radius for both batches is 250 Å.
Another possible difficulty is the presence of voids, resulting in a third constituent. Because the compacting pressure was determined by pressing pure KCl until a clear wafer was produced, one can infer that the size of any void or other crystal defect was significantly under 5000 Å (the wavelength of visible light). Measurements of the density of pressed KCl differed from bulk values by less than 0.2%, suggesting that the concentration of voids is indeed small.

One question that still remains concerns the thickness of oxide coatings on the grains. Besides changing the effective grain size and volume fraction of metal in a composite, it also affects the geometry by preventing so-called "closest approaches" between grains. There are presently no quantitative measurements of the oxide thickness. However, if one attributes the brown color of some of the smokes to a thicker oxide coating, it is then possible to divide the smokes into two categories with either a high or low level of oxidation.
Sample preparation - films

In this section the preparation of granular lead films will be discussed. These films were produced by the technique of ion beam sputter deposition. The method starts with a sapphire wafer having optically flat parallel sides, 5/8" in diameter and 1mm thick. The wafers were cleaned using acetone followed by freon in an ultrasonic cleaner. The last traces of freon were "blown off" to minimize any residue. Next, copper contacts were deposited in a configuration suitable for 4-probe resistance measurements. These contacts consisted of two sets of two parallel strips near opposite edges (fig. 7). The copper contacts, produced by sputter deposition, were found to be very sturdy, allowing for wires to be soldered directly.

Substrate mounting

The next step was to deposit the lead. A special adaptation for the substrate holder was designed to allow for resistance measurements of the film during deposition (see fig. 8). The bottom aluminum ring served to center the sapphire wafer while the top ring provided an aperture which masked the extreme edges of the substrate. This left a small portion of the copper contacts uncoated for later use. Gold coated copper strips were used to
Figure 7. Film sample substrate contact geometry. The circular dashed line indicates the outer edge of where the film will be deposited.

**TOP VIEW**

**CROSS SECTIONAL VIEW**

- a – sapphire substrate
- b – copper substrate contacts
- c – masking ring
- d – mylar insulating rings
- e – copper contact clamps
- f – centering ring
- g – mounting base

Figure 8. Substrate holder for measurement of sample resistance during film deposition.
connect to the substrate contacts. These strips were insulated from the other parts of the substrate holder by mylar sheets. The substrate assembly was then mounted in the ion mill and wires were connected to the copper strips. These wires passed through a vacuum feedthrough to an external circuit for measuring the resistance.

Resistance monitoring

An AC lock-in technique was found necessary due to the harsh electrical environment inside the bell jar during deposition. This simple circuit (fig. 9) uses the reference output of a PAR model 126 lock-in amplifier (0.5 V rms). The circuit serves to divide down the voltage (50 \( \mu \)V rms) and limit the current to 1 \( \mu \)A. With this setup, the voltage applied to the series combination of 10 kohm and sample resistance is essentially constant, independent of the sample's resistance. The resistance of the sample is now a simple function of the voltage across the sample,

\[
R_{\text{sample}} = \frac{V_{\text{sample}} \text{(\( \mu \)V)}}{(50\mu\text{V} - V_{\text{sample}} \text{(\( \mu \)V))) \times 10 \text{kohm}} (13)
\]

The voltage across the sample was measured using the lock-in. A frequency of approximately 1 kHz was found to work well. The specific frequency used depended most
Figure 9. Circuit for performing AC sample resistance measurements during ion sputter deposition.
strongly on the magnetic field used in the ion gun, suggesting that most of the interference was due to radiation from charged particles in orbits around magnetic field lines.

Ion mill technique

The ion mill system was initially evacuated to a pressure below $5 \times 10^{-6}$ Torr. Next, the flow of argon gas was started. A Veeco model APC-110 pressure controller was used to maintain a pressure of $8 \times 10^{-5}$ Torr in the bell jar. A stable argon ion plasma was established in the gun assembly as follows. First, a current of about 20 A was applied to a cathode in the plasma region. A potential of 40 V between the cathode and the walls of the chamber was then usually sufficient to produce arcing. A magnetic field, produced by a current of 0.8 A through the field coils, increased the ion density and stability of the plasma. The entire plasma chamber was now raised to a high DC voltage, causing ions to be accelerated through a set of grid apertures toward the target, which was at ground potential. The grids produced a well collimated, uniform ion beam. Temporary shut down of the ion beam could be accomplished by turning off the magnetic field. Turning the field back on usually brought the beam back.
Before lead film deposition, the substrate surface was ion etched for approximately 30 seconds to remove the oxide from the copper contacts and any residual surface contaminants. The substrate holder was then removed from the beam and placed behind a shutter. The beam was turned on the target, also for 30 seconds, to remove any oxide layers from it. The shutter was removed from in front of the substrate and the ion beam turned on. Deposition geometry is shown in figure 10. In this geometry, the accelerated ions collided with the target causing atoms to be sputtered off. These atoms then collected on the substrate to form a film. Ion beam parameters are shown in table 2. The deposition time required to detect a change in the voltage across the sample (i.e. the sample is just beginning to conduct) varied from sample to sample but 15 minutes is a typical time. At this point the sample's resistance dropped rapidly as deposition continued. When a desired resistance was reached, the beam was quickly shut off.

Were the film exposed to the atmosphere at this point, the lead would oxidize and its resistance would change (possibly becoming infinite). For this reason, a transparent, insulating layer was deposited onto the film from a fused quartz plate target.
Figure 10. Ion mill deposition geometry.
Table 2. Ion beam operating parameters

<table>
<thead>
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<th></th>
<th>Pb deposition</th>
<th>Silicon oxide deposition</th>
<th>First 5 min.</th>
<th>Remainder</th>
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<td>Arc voltage</td>
<td>40V</td>
<td>25V</td>
<td>35V</td>
<td></td>
</tr>
<tr>
<td>Arc current</td>
<td>0.64a</td>
<td>0.3a</td>
<td>0.5a</td>
<td></td>
</tr>
<tr>
<td>Cathode voltage</td>
<td>6.5V</td>
<td>6.7V</td>
<td>6.7V</td>
<td></td>
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<tr>
<td>Cathode current</td>
<td>17a</td>
<td>18a</td>
<td>18a</td>
<td></td>
</tr>
<tr>
<td>Magnet voltage</td>
<td>14V</td>
<td>14V</td>
<td>14V</td>
<td></td>
</tr>
<tr>
<td>Magnet current</td>
<td>0.41a</td>
<td>0.41a</td>
<td>0.41a</td>
<td></td>
</tr>
<tr>
<td>Accelerating voltage</td>
<td>1.0kV</td>
<td>750kV</td>
<td>850kV</td>
<td></td>
</tr>
<tr>
<td>Accelerating current</td>
<td>12ma</td>
<td>6ma</td>
<td>18ma</td>
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</tr>
<tr>
<td>Target current</td>
<td>9.3ma</td>
<td>2.8a</td>
<td>3.0a</td>
<td></td>
</tr>
<tr>
<td>Neutralizing current</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The ion beam parameters were similar to those used for the Pb deposition except for the inclusion of beam neutralization. The positively charged argon ions require a source of electrons at the target with which to combine, otherwise the target will become positively charged. The beam would then no longer be accelerated toward the target and deposition would essentially stop. Normally, the target was conducting and a source of electrons was provided by the accelerating power supply. In the case of the definitely non-conducting quartz, an electrically heated filament in the beam provided the source of electrons. When the target began to show a positive charge, these electrons were attracted to the surface where they neutralized the positive charge.

The silicon oxide deposition was usually started slowly, using a lower beam current and accelerating potential. Also, the substrate was moved back somewhat from the target. This technique tended to avoid major changes in the sample's resistance, probably by preventing excessive heating of the substrate which would allow for topological changes in the lead grains (i.e. "beading up"). After an initial layer was deposited (typically 5 minutes), the beam intensity and deposition rate could be increased without change in the sample. The deposition continued until a hazy sky blue color appeared on the surface. After a period of cooling, the
bell jar was vented and the substrate holder, with sample, removed. Despite these precautions, those samples which were of a high resistivity were occasionally susceptible to change for a period of time after deposition. Some films would suddenly show a drop in the resistivity while other would become totally insulating. This may have been due to the actual act of measuring the sample's resistance. The electrical resistance is likely dominated by a few weak junctions between island grains. A small measuring current appears as a large current density at a narrow junction. The resistive heating may either cause the junction to "open" or fuse the two grains together. In one case, the resistance would go up, while in the other, it would go down. The result in either case is a more stable sample.

Characterization - Films

The primary characterizing feature of these samples was their sheet resistance. The area between the electrical contacts was nearly square so that directly measured resistances were essentially the sheet resistance.

The surface topology was studied using scanning electron microscopy. It was expected that the samples, prepared as described above, would be difficult to study
Plate IV. Scanning electron micrograph of four Pb films.

a) Pb 4  \( R = 33 \ \Omega/\text{sq.} \)
b) Pb 5  \( R = 120 \ \Omega/\text{sq.} \)
c) Pb 12  \( R = 176 \ \Omega/\text{sq.} \)
d) Pb 8  \( R = 274 \ \Omega/\text{sq.} \)
with the SEM due to the insulating layer of silicon oxide over the lead. For this reason, several film samples were prepared without the silicon oxide and another was prepared with both the oxide and another very thin copper layer sputtered on top. It was found that none of these specially prepared samples produced good images. However, fairly good images were obtained from those samples which had no special treatment. This surprising result suggests several things. First, the silicon oxide is probably not too thick, at most 1000 Å. The lack of any detail from the copper coated sample suggests that the silicon oxide forms a smooth layer. The "bare" samples should have a layer of lead oxide on the grains, which may have served to lower the contrast at grain boundaries.

Electron micrographs revealed grains having varied shapes and separated by narrow voids. The topologies were usually consistent with the sheet resistance for a given film sample. Films with low sheet resistance ($R_0 < 500 \text{ ohms/Å}$) were found to have large ($> 5000 \text{ Å}$) extended grains with poorly defined grain boundaries. Films with $R_0$ in an intermediate range ($\sim 1000 \text{ ohms/Å}$) had smaller (but still irregularly shaped) grains and more definite boundaries. It was especially difficult to get good images for the films with the highest values for $R_0$. One which did produce a good image had much smaller
(a<1000 Å), more nearly spherical, grains.

V vs I measurements on granular films

Voltage versus current measurements were made to further characterize the film samples. This section describes the experimental technique, results and interpretation of these measurements. Only samples after no. 6 were studied as earlier samples had evaporated gold contacts which did not adhere to the sapphire.

A simple probe was constructed for use in a liquid helium cryostat. It consisted of a copper sample stage at the end of a low thermal conductance stainless steel tube. The sample stage housed a calibrated carbon glass resistance thermometer (Lake Shore Cryotronics model CGR-1-15000) and a heater consisting of 100 ohms of manganin wire (11.31 ohms/ft.) wound non-inductively. The stage was designed to hold up to four samples in shallow depressions on its surface.

Samples were attached to the sample stage using stiff vacuum grease to improve thermal anchoring. A carbon based grease was preferred since it is more easily removed with organic solvents (i.e. acetone) than a silicon grease. Indium was used to solder wires to each of a particular sample’s four copper contacts.
Using the standard 4-probe technique, current was applied to the outer contacts and the voltage produced was detected across the inner contacts of the sample. Measurements at $T=300K$ (room temperature), $T=77K$, and $T=7.5K$ (for lead, $T_C=7.2K$) revealed a linear relation between voltage and current, indicating strictly ohmic behavior. At temperatures below 7.2K, the behavior changed significantly (figs. 11-13). For most samples, the voltage no longer increased smoothly with increasing current, but instead appeared in discrete steps. Most samples were also hysteretic, following a different $V$ vs $I$ curve depending on whether the current was being ramped up or down. The samples of lower sheet resistance were typically found to be superconducting for temperatures well below 7.2K. Critical currents were on the order of milliampere. As the temperature was increased towards 7.2K, the critical currents decreased toward zero. Also, a given voltage step decreased in size while occurring at a lower current.

The resistive transitions as a function of temperature were also investigated (fig. 14). Typically, the resistance dropped suddenly at 7.2K, but not immediately to zero but instead showed a resistive tail sometimes extending down as far as 4.5K (actually, film no. 8 showed a tail which extended below the range of
Figure 11. Voltage vs. current curves for Pb #6 at T=1.5 K. Arrows indicate the direction the current is being ramped.
Figure 12. Voltage vs. current curves for Pb #7 at T=1.5 K. Arrows indicate the direction the current is being ramped.
Figure 13. Voltage vs. current curves for Pb #8 at T=1.5 K. No hysteresis was observed.
Figure 14. Resistive transition for a granular lead film. $T_c$ (bulk) for lead is 7.19 K.
temperatures available in the cryostat). Using the value for the resistance just above 7.2K and the room temperature resistance, one can calculate the residual resistivity ratio (RRR). Values for this ranged from 30 down to near unity with the majority less than 10. This suggests that much of the resistance is due to scattering from imperfections, an essentially temperature independent process which is accord with the granularity of these films.

The results discussed here are in generally good agreement with previous measurements on granular superconducting films\textsuperscript{25,26}. The non-linear V vs I dependence has been interpreted using a coupled Josephson junction model. The voltage steps are due to reaching the critical current of a particular junction between superconducting regions. Each of these regions couples to (i.e. becomes phase coherent with) its neighbors at different temperatures which depend on the strength of the coupling interaction. The variation in coupling strengths accounts for the long resistive tails. Overall, the films of low sheet resistance can be described as having more strongly coupled grains and larger regions over which the superconducting phase does not vary. The films of high sheet resistance have poorly coupled grains.
CHAPTER IV

EXPERIMENTAL TECHNIQUE

This section describes the methods used to determine experimentally a particular sample's response to far infrared radiation. The frequency region of interest is one for which spectroscopic measurements are particularly difficult due to the lack of high power sources and good detectors. The use of an interferometer rather than a monochromator helps to overcome this difficulty to some extent.

Interferometry

The technique of fourier transform interferometry has been discussed in a number of books and articles\(^2\),\(^7\),\(^28\); only a brief discussion will be given here. An interferometer is a device which divides light from a source into two parts, introduces a known phase difference between these parts, and then recombines them. The phase difference is achieved by allowing the light to traverse different distances before being recombined. The actual phase difference is then a function of the wavelength of light used. The signal intensity which
results is a complex function of the path difference. It has been shown that this signal intensity is the Fourier transform of the spectral intensity distribution.

\[ I(\sigma) = \int_{-\infty}^{\infty} S(\omega) e^{-2\pi i \sigma \omega} d\omega + I(\infty). \]  \hspace{1cm} (14)

where \( \sigma \) is the path difference, \( \omega \) is the frequency (measured in units of inverse length), \( S(\omega) \) is the spectral intensity distribution of the radiation, and \( I(\infty) \) is the signal intensity for infinite path difference. An expression for the spectral intensity distribution can be obtained from the inverse Fourier transform. The result is,

\[ S(\omega) = \int_{-\infty}^{\infty} [I(\sigma)-I(\infty)] e^{2\pi i \omega \sigma} d\sigma. \]  \hspace{1cm} (15)

From these expressions, it would appear one would need to know the intensity for a continuum of path differences from \(-\infty\) to \(+\infty\). This knowledge is obviously impossible so that one resorts to a finite number of measurements between zero and some maximum path difference. Two problems occur from this approximation. First, the maximum total path difference results in loss of resolution and the appearance of side lobes near sharp spectral structures. The side lobes can be handled using the technique of apodization. This investigation was
not concerned with detailed structure so the loss of resolution was of no great consequence. The second problem is due to the discrete sampling which gives rise to an effect known as aliasing. This problem was overcome in the standard way using filters to remove the higher order frequencies that would otherwise produce erroneous results.

Experimental set-up

A lamellar grating interferometer was used to make the spectral measurements in this investigation (fig. 15). Figure 16 illustrates a portion of a lamellar grating showing how a path difference is achieved between portions of the incident radiation. This instrument provides better interferometric modulation than a Michelson type interferometer in the very far infrared due to poor beam splitter efficiency of the Michelson. A mercury arc lamp served as source. Brass tubing (1/2" I.D.) was used as "light pipe" to guide the radiation through the instrument. The entire interferometer was enclosed in a vacuum tank to prevent atmospheric absorption due primarily to water vapor.

A liquid helium cooled bolometer was chosen for detection of the far infrared radiation. The cryostat used for this was also used to cool the samples being
Figure 15. Schematic diagram of the lamellar grating interferometer.
Figure 16. Two views of the lamellar grating showing how an optical path difference is achieved.
investigated. Figure 17 shows the cryostat geometry. The detector was a doped germanium semiconductor and was attached to a bath of liquid helium which was cooled, by pumping, to 1.2K. A vacuum space thermally isolated the detector region from the remainder of the cryostat. Outside the detector vacuum jacket was a set of filters used to provide the high frequency cutoff necessary to avoid aliasing.

This same cryostat served to cool the samples. Brass light pipe brought the radiation down to the sample stage. Figure 18 shows a detailed diagram of the sample stages for both transmission and reflection measurements. Openings through the stage allow for the passage of radiation. A sample to be studied is clamped over such an opening. For transmission measurements, the stage allowed for measurements to be done on three samples and left one opening blank for background signal measurement. For reflection, there was a single sample, and a mirror for background measurements. These sample stages could be easily interchanged in the cryostat. For both the transmission and reflection apparatus, the stage is made of OFHC copper and houses two Allen-Bradley resistors (580 ohm and 3.3 kohm) which were used as thermometers. One lead of each resistor was soldered to the copper stage for good thermal contact. These resistors have been shown to have temperature dependent resistances
Figure 17. Schematic of cryostat used in cooling the samples and detector for infrared measurements.
Figure 18. Diagram showing multiple internal reflections reflections in composite.

Figure 19. Schematic of reflection apparatus. Lengths of light pipe are actually longer than shown to reduce polarization effects.
which follow the relation,

\[ T = \frac{\log_e(R)}{[a \log_e(R) + b]^2}. \]  

(16)

Here, \( R \) is the resistance measured at temperature \( T \) while \( a \) and \( b \) are constants. Resistance measurements were made on each resistor while they were immersed in liquid nitrogen (77K), liquid helium (4.2K) and also in pumped liquid helium. The constants \( a \) and \( b \) were determined from the resistance values at \( T = 77K \) and \( T = 4.2K \). Temperatures for the pumped helium could then be calculated. For the pumped helium liquid, a Wallace and Tiernan model 6IC-1D-0050 gauge was used to measure the vapor pressure above the liquid surface. From these measurements, the temperature of the helium bath could be determined from vapor pressure tables. A comparison of temperatures as determined by both resistance thermometry and vapor pressure thermometry showed agreement within a few percent (table 3).

A resistance-wire heater was wound non-inductively around the rim of the sample stage using about 10 ft. of 11.31 ohm/ft. manganin wire. Wiring to this heater and the resistance thermometers was accomplished with 40 ga. copper wire for low thermal conductance. Connections were made through a vacuum feedthrough at the top of the cryostat.
Table 3. Resistance thermometer values

<table>
<thead>
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<th>Constants</th>
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</thead>
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<tr>
<td>300K</td>
<td>77K</td>
</tr>
<tr>
<td>Resistor</td>
<td></td>
</tr>
<tr>
<td>680 ohm</td>
<td>655 ohm</td>
</tr>
<tr>
<td>3.3 kohm</td>
<td>3.23 kohm</td>
</tr>
</tbody>
</table>

At lowest temperature,

helium vapor pressure = 11.0 mm => 1.77 K

680 ohm resistor = 6.90 Mohm => 1.81 K

Resistance set points for normal state measurements

<table>
<thead>
<tr>
<th>680 ohm</th>
<th>3.3 kohm</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>2.15 kohm</td>
<td>9.82 kohm</td>
</tr>
<tr>
<td>Pb</td>
<td>4.3 kohm</td>
<td>18 kohm</td>
</tr>
</tbody>
</table>
For the transmission apparatus, brass light pipe below the sample stage carried the radiation down to the detector. For the reflection apparatus, a beam splitter was used to carry some of the reflected radiation around the sample and then on to the detector.

The radiation from the interferometer exits through light pipe which terminates in a polyethylene window. The entrance to the light pipe of the detector cryostat has a similar window. The detector/sample cryostat was placed up against the vacuum tank of the lamellar grating interferometer such that these two windows were aligned with each other. At this point the cryostat and interferometer were rigidly clamped together. Before measurements were made, the entire system was suspended on a set of air shocks to reduce the effect of building vibrations.

Low temperature procedure

Samples were mounted on the sample stage and placed in the cryostat after which liquid nitrogen was placed in the outer dewar. The system was then allowed to cool to 77K overnight. Liquid helium was introduced the next day. After filling the detector reservoir and sealing the filling valve, pumping on this bath was initiated. The detector bath was pumped to its limiting temperature
of 1.2K and was held there for the remainder of the experiment. Pumping was also started on the entire helium reservoir. It should be noted that the pumping systems for each of these reservoirs were entirely isolated so that their temperatures were essentially independent. The main reservoir reached a limiting temperature of 1.8K. Measurements for samples in the superconducting state were done with the samples immersed in the main reservoir. This immersion assured that their temperatures were well below $T_c$. For the normal state measurements, the helium level was allowed to drop below the sample position and heat was applied through the manganin wire resistance heater until the temperature was well above $T_c$. An Artronix model 5201-E temperature controller was used to maintain this temperature by referencing the 680 ohm resistance. Table 3 shows the resistance values and corresponding temperatures used.

Infrared signal measurement

The detector element was biased using a battery supply. The voltage appearing across the detector was fed to the input of an Ithaco model 393 lock-in amplifier. The source was turned on and the appropriate filter(s) was moved into place. The blank opening at the sample stage was placed in the optical path. At this
point, signal was usually observed on the lock-in. By adjusting the bias voltage, filter alignment and chopping frequency, the signal to noise ratio could be maximized.

The technique used is known as step and integrate. The path difference was changed in discrete steps and the signal at each point was measured over a certain time interval. The movable part of the grating was moved by a micrometer driven by a stepping motor, which provided reasonably accurate changes in path difference. Because the interferometric signal was symmetric on both sides of zero path difference, it was necessary to measure the interference pattern on one side only. For the transform of this signal to yield the correct spectrum, it was critical to start at zero path difference and change the path difference very accurately. Because zero path difference was the only point where all frequencies interfere constructively, this point could be found by searching for maximum signal. This point is often referred to as the "white light position". Also, because the interference pattern should be symmetric about this point, one could look at one step on either side and make fine adjustments until equal signal was observed. The instrument was now symmetrized. The signal was measured by feeding the output of the lock-in into an integrating digital voltmeter. This device sampled the voltage over a given time period (typically 4 seconds) and then sent
the information, in digital form, to a card punch where it was recorded on computer cards. After recording a point, the grating was stepped to the next position and the measuring process was repeated. Data was taken until the total path difference was sufficiently large so as to produce 1 cm⁻¹ resolution. This was typically 64 points for a spectrum designed to be cut off at about 60 cm⁻¹. The set of data thus produced is known as an interferogram. Several interferograms were taken for each sample at each temperature. Background measurements were taken at frequent intervals to correct for any possible changes in source intensity or detector sensitivity.

Data processing

The cards of punched data were fourier transformed using an Amdahl 470 computer. The spectra for a given sample at a given temperature were averaged to produce a final spectrum for each. A standard deviation at each point was also computed. Each sample spectrum was divided by an appropriate background spectrum to produce a transmission ratio. For film measurements, this was the desired quantity. For the composites, an absorption coefficient was computed using,
\[ \alpha(\omega) = -(1/x) \log_e(T(\omega)) \]

\[ x = \text{sample thickness} \] (17)

For reflection measurements, the ratio of sample to background (a brass mirror) yielded the reflection coefficient. All these results were then output both graphically and numerically. At this point, noisy or poor quality data were discarded. The remainder was entered into a PDP 11 computer for further processing.
CHAPTER V

ANALYSIS

Composites

This section describes the methods used to compare the experimental results with the theoretical predictions. The absorption coefficient for the composites, as determined in the last section, must still be corrected for the effects of reflections from the surfaces of the sample. If one considers the effects of multiple internal reflections, then an expression for the transmitted intensity is actually a sum of individual components, each having undergone an additional internal reflection (fig. 18). This expression can be summed into a closed form to yield,

\[
T = \frac{(1-R)^2 e^{-\alpha x} e^{ikx}}{1-R^2 e^{-2\alpha x} e^{-2ikx}}. \tag{18}
\]

(66)
where \( T \) is the transmitted intensity, \( R \) the reflection coefficient, \( x \) is the sample thickness, and \( \alpha \) is the sample's absorption coefficient. It will be shown that a typical value for the reflection coefficient is 20%. This value, along with the magnitude of \( \alpha \), allows neglecting of the term

\[
R^2 e^{-2\alpha x} e^{-2ikx}
\]

in the denominator. Also, the measurements were done in low enough resolution so that the interference term effectively averages to unity. With this, the expression can easily be turned around to yield for the absorption coefficient,

\[
\alpha = -(1/x) \log_e(T) + (1/x) 2 \log_e(1-R)
\]

This equation suggests that the previously calculated absorption coefficients should be corrected for the reflectance using equation 20. A discussion of the results of reflection measurements follows first.

Reflection results

Because of the geometry of the reflection apparatus, more than 75% of the incident signal is lost compared to
the transmission set up. This, along with the rather low reflectances of these materials, made accurate measurements difficult. For this reason, only a few samples were measured this way. As with the transmission measurements, multiple internal reflections can occur. However, except at the lowest frequencies, the samples were very absorbing so that the reflection was dominated by the front surface only. At frequencies near zero, the samples were more transparent. Reflection from the back surface then occurred causing increased total reflection and some interference patterns.

Figure 20 shows the reflection of a composite of tin (3% by volume) in KCl measured with the tin normal \( T = 25K \). The main feature is that the reflectance is essentially independent of frequency. The apparent increase in reflection at low frequencies is due to reflection from the back surface. A measurement on the same sample with the tin superconducting \( T = 1.8K \) yielded no significant difference. Measurements on samples with volume concentrations of \( f = 15\%, 17\%, \) and \( 100\% \) also revealed frequency independent reflectances. As shown in figure 20, these samples were opaque even at the lowest frequencies so that the reflectance showed no reflection from the rear surface. These samples also showed no detectable temperature dependence associated with superconductivity (fig. 21).
Figure 20. Measured reflectance for three Sn in KCl composites and one sample pressed from pure Sn smoke.
Figure 21. Ratio of the superconducting reflectance to the normal state reflectance.
Corrections to the absorption coefficient

Correction for the reflectance is now a much simpler matter since the correction term is essentially a constant, independent of frequency. The composite of 3% tin 2 in KCl was measured in both reflection and transmission. Correcting for the reflectance shifted the absorption coefficient down such that the absorption extrapolated to zero at zero frequency. Since these low concentration composites were not conducting, it should be expected that they should be non-absorbing in the limit of zero frequency. Those samples for which no value for the reflectance was available were then corrected by fitting the normal state absorption coefficient to the function,

\[ \alpha(\omega) = K\omega^2 + B. \]  \hspace{1cm} (21)

A good fit was obtained for the majority of the composites, which is not surprising since the theory predicts such a frequency dependence and previous measurements on granular composites have shown this same frequency dependence. The value for \( B \) was then interpreted as due to the reflectance and was subtracted from both the normal state and superconducting state absorption coefficients.
Figure 22 shows the corrected absorption coefficient for two composites of tin in KCl, one with a volume fraction, \( f \), of 0.75% and the other with \( f \approx 3\% \). Both composites were made from the same batch of tin smoke having a mean radius of 150 Å. Two curves are shown for each composite, one with the temperature above \( T_c \) and the other well below \( T_c \). This data was typical of most of the composites measured. The normal state absorption coefficient increases quadratically with frequency, with the higher concentration sample being more absorbing. The magnitude of the absorption should be compared to that predicted by the theory as given in figure 5. The experimental absorption was measured to be several orders of magnitude larger than the theoretical prediction. This result agrees with much of the earlier experimental work where similar discrepancies have been observed. The superconducting absorption coefficient is similar to the normal state absorption except for the appearance of increased absorption for frequencies around \( \omega = 10 \text{ cm}^{-1} \). The spectroscopic energy gap, \( 2\Delta \), corresponds to 9.3 cm\(^{-1} \) for tin. Figure 22 shows the corrected absorption coefficient for two tin composites having the same metallic concentration but made from two different batches of smoke. The one batch had a mean particle radius of 150 Å while the other had a mean radius of 50 Å. Again, the absorption is shown for temperatures
Figure 22. Absorption coefficient for two Sn in KCl composites having different metal concentrations and at temperatures above and below $T_C$. 
Figure 23. Absorption coefficient for two Sn in KCl composites having the same metal concentration but different mean grain size. Results for temperatures above and below $T_c$ are shown.
Figure 24. Absorption coefficient for a typical Sn in KCl composite above and below \( T_c \).
both above and below $T_c$. The normal state absorption can be seen to increase with particle size. The superconducting absorption still shows the absorption "knee" for frequencies around 10 cm$^{-1}$).

As discussed earlier, the absorption coefficient was fitted to a quadratic form. The value for the coefficient, $K$, was then a measure of the absorption in the normal state. Table 4 shows the value of $K$ for each tin composite measured, along with that particular sample's other characteristics. For a set of composites made from the same batch of smoke, the value for $K$ showed some scatter, but overall was constant to within an order of magnitude. For a given concentration, there appears to be no definite size dependence to the absorption. This may be due to the varying amount of oxide on the grains. Smoke batch 6 had a very brown color suggesting that those grains were highly oxidized. A composite made from highly oxidized smoke would have effectively smaller grains and lower metal concentration. Such a composite would be less absorbing which is the case for composites made from smoke batch 6.

The observed absorption increase for composites of granular superconductor was totally unexpected. Figure 25 shows the temperature dependence of the transmitted signal through one of the composites. This measurement was done with the interferometer at the white light
<table>
<thead>
<tr>
<th>Smoke</th>
<th>Radius (Å)</th>
<th>Metal conc. (f in %)</th>
<th>K (x10^{-3} cm)</th>
<th>Kf (x10^{-3} cm)</th>
</tr>
</thead>
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<tr>
<td>Sn 10</td>
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<td></td>
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<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>73</td>
<td>24</td>
</tr>
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<td>0.53</td>
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</tbody>
</table>

* - denotes brown Sn smokes (higher oxidation)
Figure 25. Broadband transmission as a function of temperature for a composite of Sn in KCl.
position so that a wide band of frequencies were incident on the sample. The signal is essentially independent of temperature above $T=3.7\text{K}$. As the temperature dropped below this value, the signal decreased indicating the onset of the absorption increase. The bulk superconducting transition temperature for tin is $3.7\text{K}$ thus providing strong evidence that the absorption increase is associated with the grains becoming superconducting.

The frequency dependence of the absorption increase can best be seen by subtracting the normal state absorption from the superconducting state absorption. Normalizing this result by dividing this by the coefficient $K_f$ for the sample resulted in a nearly universal (i.e. typical of all the tin composites studied) curve (figures 26, 27). The only difference noted was that the size of the absorption increase was slightly less for those samples made from the brown smokes. As the frequency increased beyond $10\text{ cm}^{-1}$, the absorption increase tended to zero (i.e. the superconducting absorption approached the normal state absorption). The results for frequencies below $8\text{ cm}^{-1}$ were unclear because of the rapid loss of signal at low frequencies. However, results for some of the tin composites suggested that the superconducting absorption was much less than the normal state absorption in this frequency range.
Figure 26. Normalized relative absorption coefficient for two Sn in KCl composites.
Figure 27. Normalized relative absorption for a Sn in KCl composite.
Lead and Niobium composites

Composites made using lead and niobium were also studied to see if the absorption increase described above was a general property of superconductors, or peculiar to tin. Also, the energy gap is much larger in these metals which would allow for more accurate measurements of the superconducting absorption for frequencies below the gap. Niobium was tried first because it is a hard metal which would not deform in the pellet making process. However, as described earlier, the niobium was not produced by inert gas evaporation, but by grinding and sifting of niobium powder. Figure 28 shows the normal state absorption for a composite of Nb in KCl. Again, the absorption increases quadratically with frequency. Figure 29 shows the change in the absorption due to superconductivity. There is an increase in the superconducting absorption around the gap for Nb (24.6 cm\(^{-1}\)), but the increase is only of the order of 10% of the normal state absorption. For tin, the increase was nearly 100% over the absorption in the normal state. This may be due to the niobium grains being roughly two orders of magnitude larger than the tin grains.

The results for a composite of Pb in KCl are shown in figure 30. The normal state absorption increased quadratically with frequency as usual. Figure 31 shows
Figure 28. Normal state absorption coefficient for a composite of Nb in KCl.
Figure 29. Relative absorption coefficient for a composite of Nb in KCl.
Figure 30. Normal state absorption coefficient for a composite of Pb in KCl.
Figure 31. Relative absorption coefficient for a composite of Pb in KCl.
the change in absorption associated with superconductivity. The energy gap for Pb corresponds to 22.0 cm\(^{-1}\). The absorption increase is clearly visible for frequencies at and above the gap. The signal to noise is also good for frequencies below the gap where it can now be seen that the superconducting absorption is much less than in the normal state.

Summarizing the results for the composites, the normal state absorption increased quadratically with frequency for all metals measured. The absorption also increased with increasing metal concentration. The dependence on size was not clear. In the superconducting state, the absorption was less for frequencies below the energy gap. For frequencies at and just above the gap, the absorption is larger than in the normal state. As the frequency continued to increase, the absorption approached that of the normal state. The composites of tin showed the largest effect, with the superconducting absorption being nearly double the normal state absorption just above the gap frequency. The size of the absorption increase was found to scale linearly with the overall magnitude of the normal state absorption for a given composite. The niobium showed the least effect.

An interesting feature of the composites is the change from insulating behavior at low metal concentrations to metallic behavior at higher
concentrations. These composites have been shown to make such a transition at metal concentrations of approximately 20%. The effect that such a drastic change in the electrical properties has on the superconducting absorption should provide useful information as to its source. However, infrared measurements for the composites were limited to those samples for which the metallic concentration was under 5%. Samples with higher metal concentrations were too absorbing and could not be made thin enough to allow for transmission measurements.

Transmission measurements - lead films

Films of granular metal provided a system where the overall properties could be varied from metal-like to insulator-like while still allowing for infrared measurements. However, the granular metal film system is inherently different from the composite system. The primary difference is due to the 2-dimensional nature of the films. Also, the grains are much more irregularly shaped. The field each grain sees and how it interacts with it will reflect these differences. Still, effects due to isolated small grains should still be present.

The granular films could not easily be characterized by the metal concentration nor grain size. The feature which tended to define the properties of a given film was
its sheet resistance. However, even this was not ideal for relating to the optical properties for the following reason. The far infrared radiation sampled over an area the size of the wavelength. The measured transmission was then an average of these areas over the entire sample. On the other hand, the DC electrical resistance can depend strongly on the anisotropies of the film. As an example, consider a system consisting of one narrow conducting strip across the sample, the remainder of the sample being transparent. The measured DC resistance would be quite low, while the transmission of radiation would be rather large.

Film transmission - normal state

Figure 32 shows the far infrared transmission for three granular lead films. These films are labeled according to their measured DC sheet resistance. The transmission of a thin film on an insulating substrate can be related to the sheet resistance of the film using an expression due to Glover and Tinkham\textsuperscript{16},

\[ T = \frac{1}{1 + \left( \frac{\sigma d}{Z_0/(n+1)} \right)^2} \]  \hspace{1cm} (22)

where \( \sigma \) is the sample's conductivity, \( d \) is its thickness (so that \( \sigma d \) is the conductance per unit area; the sheet
Figure 32. Normal state transmittance for three granular Pb films sapphire substrates.
resistance being the inverse of this), \( n \) is the index of refraction for the substrate, and \( Z_0 \) is the impedance of free space (377 ohm). The transmission of films with low resistance was found to be small and frequency independent. This implied that the conductivity was also frequency independent, in agreement with a simple Drude model for a very dirty metal. The films with higher resistances were typically more transparent. Also, the transmitted intensity began to show a dependence on frequency, with the transmission decreasing as the frequency increased. This represents a deviation from a classical Drude model and typical metallic behavior. The data for the most transparent film shown (# 7) also shows some oscillations. These have been attributed to interference from multiple internal reflections in the substrate. Though the substrates were all of nearly the same thickness and cut along the same crystal axis, not all the samples showed this interference pattern. The reason for the difference is not clear.

Film transmission - superconducting state

The expected transmission can be readily calculated using equation 22, above, and the expressions for the frequency dependent conductivity (equations 10,11). This transmission has been calculated and the results are
plotted for the type II coherence factors and also without coherence in figure 33. The first comment to be made is that the sharp structures around the gap frequency will not be experimentally observable due to gap anisotropies and fluctuations due to the smallness of the grains. At frequencies below the gap, the films are not absorbing (since $\sigma_{ls}(\omega)$ is zero) but are highly reflecting due to the magnitude of $\sigma_{2s}(\omega)$. As the frequency increases from zero, the reflectance drops and the sample becomes more transmitting. At and above the gap, $\sigma_{ls}(\omega)$ becomes non-zero and the transmission drops off due to absorption. The experimental transmission results for the films at 1.8K showed deviations from the normal state measurements (10 K). As for the composites, the broadband transmission was measured as a function of temperature (fig. 34) The transmission was again essentially independent of temperature down to 7.2 K. At this point, a sudden change was noted. This change has been associated with superconductivity since $T_c$ for bulk lead is 7.22 K. Unlike the composites, the change was not always a decrease in transmitted signal as can be seen in the figure. Figures 35, 36 and 37 show the ratios of the superconducting transmission to the normal state transmission for three different film samples. Film 6 was typical of those samples with low $R\square$. The superconducting to normal transmission ratio is in
Figure 33. Computed transmission ratio for $T_{\text{super}}/T_{\text{normal}}$ using type II and no coherence.
Figure 34. Broadband transmission as a function of temperature for two granular Pb films.
Figure 35. Ratio of superconducting transmission to the normal state transmission for a granular Pb film having low sheet resistance.
Figure 36. Ratio of superconducting transmission to the normal state transmission for a granular Pb film having intermediate sheet resistance.
Figure 37. Ratio of superconducting transmission to the normal state transmission for a granular Pb film having high sheet resistance.
qualitative agreement with the theoretical prediction and with previous measurements on more uniform superconducting films}. In film 10, the peak in the transmission was much smaller and was shifted to higher frequencies. Below the gap, the transmission was less in the superconducting state. Film 7 has practically no peak in the transmission but instead a minimum around the gap frequency. This behavior is in total disagreement with the theoretical predictions. The results for the films studied are compiled in table 5. The sheet resistance was calculated from the measured normal state transmission at the gap frequency (22 cm\(^{-1}\)) using eq. 22. Also included, if measured values were available, are the values for the residual resistivity ratio (RRR) and the critical current of each sample. The RRR is the ratio of a sample's resistance at 4.2 K to that at room temperature (300 K). Since lead becomes superconducting at 7.2 K the value of the resistance just above \(T_c\) was used instead. The critical currents were a measure of the superconducting coupling between the grains along the current carrying path. If the overall infrared transmission in the superconducting state was in agreement with the results of the Mattis and Bardeen calculation (equations 10, 11) it was classified as type B (for BCS). If the infrared transmission was not in agreement, it was labeled A (for anomalous). Those
### Table 5. Film results

<table>
<thead>
<tr>
<th>Pb film</th>
<th>R (22\ \text{cm}^{-1}) (ohm/sq.)</th>
<th>R (dc) (ohm/sq.)</th>
<th>(\bar{R}R)</th>
<th>I(_c) (mA)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>25</td>
<td>12</td>
<td>5</td>
<td></td>
<td>B</td>
</tr>
<tr>
<td>4</td>
<td>33</td>
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</tr>
<tr>
<td>6</td>
<td>35</td>
<td>31</td>
<td>28</td>
<td>16</td>
<td>B</td>
</tr>
<tr>
<td>10</td>
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<td>120</td>
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</tr>
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<td>A/B</td>
</tr>
<tr>
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<td>2280</td>
<td>115</td>
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<td>B</td>
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</tbody>
</table>
samples which showed both a peak at higher frequencies and a dip at lower frequencies were labeled A/B. The table is listed in order of increasing film resistivity.

With this table it is possible to summarize the results of the film measurements. A sample with low $R_\square$ will have a normal state transmission which is rather small and independent of frequency. It will go superconducting and have a good size critical current. The superconducting transmission will be in agreement with the Mattis Bardeen calculations. On the other hand, a sample with high $R_\square$ will show a fairly large frequency dependent transmission in the normal state. If it goes superconducting, it will have a small critical current. The transmission in the superconducting state will be of the anomalous type.
CHAPTER VI

DISCUSSION OF RESULTS

The primary result of this experimental work was the discovery of an increase in the far infrared absorption for a granular superconductor. This absorption appears as a knee around frequencies at and slightly above the energy gap frequency for the superconductor. The superconducting absorption increase occurs for samples with reasonably isolated grains. This conclusion applies to all the composites studied along with those granular films having high resistivities. The granular films having low resistivities had less isolated grains and were found to be less absorbing when superconducting.

The results for the superconducting films of low sheet resistance are in qualitative agreement with the theory described in chapter II and also with previous experimental work on more uniform films. However, the superconducting results for the films with high sheet resistance and all the composites do not agree with the
simple theory put forward in chapter II. The data suggest that as the grains become more electrically isolated from each other, the superconducting response goes from less absorbing to more absorbing than the normal state response. Before discussing possible explanations, it will first be shown that the measured absorption is consistent with a sum rule based on causality. For a given system, the optical conductivity must obey the relation \cite{31},

\[
\int_{0}^{\infty} \sigma_1(\omega) d\omega = \text{constant}.
\] (23)

Now, first consider how a bulk superconductor obeys this relation by looking at figure 3. The sum rule above implies that the area under the curve for \(\sigma_1(\omega)\) must remain a constant. When the material becomes superconducting, a gap appears in \(\sigma_1(\omega)\). This gap results in "missing area". To obey the sum rule, this area shows up as a \(\delta\)-function at zero frequency. The strength of this \(\delta\)-function is equal to the missing area. A Kramers-Kronig transformation of \(\sigma_{1s}(\omega)\) then gives the \(1/\omega\) inductive response of \(\sigma_{2s}(\omega)\). If one now considers a composite of low concentration, the material is insulating at zero frequency. The individual grains still become superconducting so that a gap in their excitation spectrum and in \(\sigma_{1s}(\omega)\) still exists. However,
this missing area can not appear at zero frequency as for a bulk material. Instead, the missing area appears as absorption at and just above the gap.

Multiple grain effects

The theories presented in chapter 2 assumed that the infrared response was due to each grain individually and did not include multiple grain processes such as photon induced tunneling. Such processes require grains which are in close proximity if they are to occur since the probability of causing an electronic transition depends on the overlap of the electron states. The electron wave functions are expected to decay quickly with distance outside the grains. For this reason, the absorption probability between two grains should drop off quickly as the distance between the grains increases.

For a superconductor, the excited states above the gap are known as quasi-particle excitations. An absorption process between two grains would then involve the tunneling of these quasi-particles. The coherence effects discussed in chapter II hinder the formation of quasi-particle excitations on a single grain. However, if the superconducting phase is uncorrelated between two grains, the coherence effects drop out. Two problems arise here. First, the probability of the phase on two
grains being correlated is dependent on the tunneling transition probability between the grains. This is the same transition probability which governs the absorption. In other words, if it is likely that a photon will induce a transition between grains, then it is likely that the phases of the grains will be correlated and the absorption will be suppressed. More importantly, the other problem is that neglecting coherence effects entirely still does not account for the data.

The discussion above does not include Josephson pair tunneling. Theoretical calculations for the frequency dependent Josephson current have been done by Reidel and in more detailed fashion by Werthamer. They both find a peak in the tunneling current amplitude at the gap frequency. Some experimental work exists which supports these results. Still, the effect observed in this study occurred even in very low concentration samples where the grains should be very isolated and such tunneling currents would be highly unlikely.

Single grain effects

In the treatment of the infrared response of a superconductor, the interaction was assumed to be that of a transverse electromagnetic wave with the electrons of the material. A transverse field is described by a
vector potential so that the form of the interaction is $\mathbf{p}.\mathbf{A}$ and the appropriate coherence factors are type II. However, if the interaction were not transverse, but longitudinal, then the form would be $p\phi$ and type I coherence factors would be appropriate. Figures 38, 29 shows the expressions for the frequency dependent conductivity using the type I coherence factors. Figures 40 and 41 show the expected composite absorption and film transmission. The agreement with the data is at least qualitatively correct. Very recent work\textsuperscript{36} has discussed how non-local effects allow the interaction to be of type I. Though the incident electromagnetic wave is transverse, the smallness of the grains allows it to interact longitudinally. The longitudinal dielectric function does show the increased absorption effects of type I coherence factors. However, it is still not clear if a longitudinal dielectric function is consistent with the normal state results.

In conclusion, the absorption of superconducting granular composites and films has been investigated. The normal state absorption for the composites was observed to be much larger than the theoretical prediction, in agreement with previous measurements on such systems. The absorption in the superconducting state was found to increase for frequencies around the superconducting energy gap frequency, contradictory to the theoretical
Figure 38. Real (dissipative) part of superconductor conductivity ratio for Sn for type I coherence factors.
Type I coherence factors

Figure 39. Imaginary part of superconductor conductivity ratio for Sn for type I coherence factors.
Figure 40. Computed absorption for a composite of Sn in KCl using the MGT. Normal state and superconducting state with type I coherence factors are shown.
Figure 41. Computed transmission ratio $\frac{T_{\text{super}}}{T_{\text{normal}}}$ using type I coherence factors for a 25% transmitting Pb film.
prediction. Transmission measurements on very granular films showed this same effect when the films were very resistive. This anomaly can be reconciled by using type I coherence factors rather than type II factors in the expressions for a superconductor's response. However, the mechanism for this is still not clearly understood.
APPENDIX A

COMPOSITE ABSORPTION DATA

This appendix includes plots of the normal state and the superconducting state absorption coefficients versus frequency for the composites. The normal state plots use the period character (.) while the superconducting state plots use the plus sign (+). Also included are plots of the normalized relative absorption between the superconducting and normal states.
$Sn_2 \quad f=1\%$
Sn2 \ f=3\%
$Sn_2 \quad f = 3\%$.
$Sn 3 \ f=2\%.$
Sn3 \( f = 2\% \)
$S_n 3 \ f = 3\%$
$\text{Sn 3 } \tau = 3\%$.
Sn 4 f = 0.2%
Sn 4  f=1%
$Sn_4 \quad f=1\%$

Graph showing the relationship between relative absorption and frequency (cm$^{-1}$).
Sn 6 \( f = 0.3 \% \)
Sn 6  \( f = 0.3 \% \)
$Sn6 \ f = 1\%$

Absorption Coeff. (cm$^{-1}$) vs Frequency (cm$^{-1}$)
Sn6 $f=1\%$
$Sn\delta, f=3\%$
Sn 6  \( f = 3\% \)
Sn7 $t = 1\%$.
Sn7 $f=1\%$

Graph shows the relationship between frequency (cm$^{-1}$) and relative absorption.
Sn 7  \( f = 2\% \)
Sn 7 \ f=2 \%.
$S_{n7} \quad f = 3\%$
Sn7  $f = 3\%$
Absorption Coeff. (cm$^{-1}$)

Sn10  \( t = 1 \% \)

Frequency (cm$^{-1}$)
$Sn\ 10 \ \tau = 3\%$
\textit{Sn 10} \quad t = 3\%
Sn II  \( f = 0.5\% \).
Sn II  \( f = 0.5 \% \).
Sn II  f = 0.75 %
$Sn II$  $f = 0.75\%$

![Graph showing relative absorption vs frequency (cm⁻¹). The graph has points scattered across the plot, indicating a trend in absorption with frequency.](image-url)
$Sn II \ f = 1\%$
Sn II  f = 1%
$Sn\ II \ f=2\%$
$Sn II \ f = 2\%$
$SnII \ f = 3\%$

Absorption Coeff. (cm$^{-1}$)

Frequency (cm$^{-1}$)
Sn II  \( f = 3\% \)
Sn II  \( f = 4 \% \)
$Sn\,ll\ f=4\%$
Pb 1    f=0.5%
Pb I \( f=1\% \)

Absorption Coeff. (cm\(^{-1}\))

Frequency (cm\(^{-1}\))
Pb 1  f=1%
Absorption Coeff. (cm⁻¹)

Pb 1  f=3%

Frequency (cm⁻¹)

0  10  20  30  40  50

0  10  20  30  40  50
Nb 1 f=1%
Nb 1 \ f=1\%
Nb 1 \( f=3\% \)
APPENDIX B

FILM TRANSMISSION DATA

This appendix includes plots of the normal state transmittance versus frequency and the ratio of the superconducting to normal state transmittance versus frequency for the granular lead films.
Pb #1
Transmission Ratio ($T_e / T_h$) vs Frequency (cm$^{-1}$) for Pb #1
Pb #3
Transmission Ratio (Te/Tn) vs Frequency (cm⁻¹)

Pb #5
Pb #9

Frequency (cm$^{-1}$)
Pb #11
Transmission Ratio ($T_e/T_n$)

Frequency (cm$^{-1}$)

Pb #12
APPENDIX C
COMPUTER PROGRAMS

This appendix contains listings of the computer programs used to produce the values for the theoretical curves. All routines were written for use on a PDP-11 computer. The program MGTSCP computes the frequency dependent absorption using the MGT. It is capable of using values for the superconducting conductivity as produced by the program INTGRT. INTGRT is a routine to compute the integral expressions of Mattis and Bardeen using Gaussian quadrature.
C PROGRAM WHICH COMPUTES THE ABSORPTION COEFFICIENT FOR SMALL PARTICLE
C COMPOSITES USING THE MAXWELL GARNET THEORY.
C
C BOTH REAL AND IMAGINARY DATA FOR EPSILON AND NU CAN BE USED.
C
C VARIABLES:
C
ABSOP = array for storage of absorption coeff's. as funct. of freq.
AKPROP = product of part. radius and propagation constant.
AREA = computed area under LNDF function for use in determining
next radius.
DELRAO = increment used in computing AREA (i.e. dx in integration)
D1 = temp. storage
D2 = temp. storage
EIN = epsilon for insulator
EMCT = epsilon for composite in Maxwell-Garnett theory
EMW = epsilon for metal in Drude model
EMW = imag. part of EMW
F = filling fraction for metal
FILIN1 = input filespec for values of sis1/sis1
FILIN2 = " " " sis2/sis1
FILOUT = output filespec for computed data
IARRAY = scaled ABSOP for plotting
INRAD = running total of # of radii used in computation
NW = # of frequencies to be calculated
POLAR = magnetic polarizability of sphere
PURIMA = PURE IMAsinary number of unit mas. (i)
RAD = radius of particle used in calc. of ABSOP
RADBAR = mean particle radius
RADLO = initial radius
RADHI = final (or stopping) radius
RADSCL = approx. # of radii to be computed (scale)
RADSIG = std. dev. of part. radii in LNDF (for inert gas grown
particles typically 1.4 < RADSIG < 1.6 )
*** RADSIG > 1.1 ***
RMNL = log(RADBAR)
SIGL = log(RADSIG)
S1R = array of values for SIG1/sIG1n
S2R = array of values for SIG2n/SIG1n
TAU = collision time for electron in particle in units of cm
TSTARE = area used to test AREA against determining next RAD
UMET = permeability of bulk metal
UMGT = computed permeability of comp. in MGT
UMS = computed permeability for a metal sphere
VFERMI = fermi velocity for metal (entering zero defaults to Sn )
W = frequency (cm-1)
WLO = start freq. (cm-1)
WHI = stop free, (cm-1)
WNC = free by which W is incremented
WPSO = square of plasma frequency (cm-1)²

ALNDF = routine to compute probability of finding a particle
in log-normal distribution (LNDF)

******************************************************************************************
** *
** PROGRAM *
** *
** ******************************************************************************************

1 FORMAT(1H1,' PROGRAM TO COMPUTE ABSORPTION COEFFICIENT
  IN MGT FOR/' SMALL PARTICLE COMPOSITES INCLUDING
  2 SUPERCONDUCTIVITY'/')

2 FORMAT(' ENTER TITLE (Put one blank in front)'
3 FORMAT('HO', 'VALUE FOR EPSILON(INSULATOR) ?'
4 FORMAT(2F10.5)
5 FORMAT(' ENTER FILLING FRACTION(1/WPSO)***2,''
6 FORMAT(' (1.5F4.4 E11.5 E11.5 E11.5 E11.5)'
7 FORMAT(F6.4 E2E11.5)
8 FORMAT(HO,' ENTER S FOR SUPERCON. N FOR NORMAL'
9 FORMAT(A)
10 FORMAT(HO,' OUTPUT FILESPEC FOR ABSORPTION COEFF. S ?'
11 FORMAT(4A4)
12 FORMAT(HO,' INPUT FILES FOR SUPERCOND. ?'
13 FORMAT(4A4)
14 FORMAT(' RADIUS (#3) = ', F8.2)
15 FORMAT(' 2E12.5)
16 FORMAT(' 1F9.2 1X,G14.6)
17 FORMAT(' ,1F9.2,1X,G14.6,1X,G14.6,1X,F5.2,1X,''
18 FORMAT(' 1X,G14.6,1X,F5.2,1X,G14.6)
19 FORMAT(HO,' VALUE FOR UMET ?'
20 FORMAT(2F10.5)
21 FORMAT(HO,' ENTER RDSC, RADLO, RADHI, RABBAR,''
22 FORMAT(' (F8.2 E8.2 E8.2 E8.2 E8.2 E8.2 E8.2 E8.2 E8.2)
23 FORMAT(' ,F8.2 )'
24 FORMAT(3F8.2)
25 FORMAT(HO,' VFORHS = E11.5,2X,WP+2=' E11.5,2X,'F=' F6.4,2X,''
26 FORMAT(' ,SUPER=',A1,'1H, 'NRO=', F8.1,2X,'RHS=', F8.1,2X,'# of rads=','
27 FORMAT(' 15,2X,'R mean=', F8.3,2X,'std. dev.', F5.3,'//')
REAL ABSORP(1000), W, TAU, RAD, E2MW, VFERMI
COMMON /PLOT/ABSORP
DIMENSION SIR(1000), S2R(1000), FILINI(4), FILIN2(4), FILOUT(4)
INTEGER IARRAY(1000)
COMPLEX*8 EIN, EMW, AKPROP, UMS, UMET, POLAR, EMECT, UMG, PURIMA, SUP
DATA PI/3.14159/
PURIMA=CMPLX(0.0, 1.0)

C
C BEGIN PROMPTS AND ENTERING OF DATA
C
27 TYPE 2
   ACCEPT 2
   TYPE 22
   ACCEPT 24, WLO, WHI, WINC
   NW=INT((WHI-WLO)/WINC)+1
   WLO=WLO-WINC
   IF (NW=1000) 29, 29, 28
28 TYPE 23
   GO TO 27
29 TYPE 5
   ACCEPT 6, F, WPLSQ, VFERMI
   IF (FERMI.LE.0.0) VFERMI=1.89E+08
   TYPE 3
   ACCEPT 4, D1, D2
   EIN=CMPLX(D1, D2)
   TYPE 7
   ACCEPT 8, SUPER
   TYPE 17
   ACCEPT 18, D1, D2
   UMET=CMPLX(D1, D2)
   TYPE 9
   ACCEPT 10, FILOUT
   IF (SUPER.NE., 'S') GO TO 40
   TYPE 11
   ACCEPT 12, FILINI
   ACCEPT 12, FILIN2

C OPEN INPUT FILES AND READ SUPERCOND, DATA
C
OPEN (UNIT=2, NAME=FILIN1, TYPE='OLD')
OPEN (UNIT=3, NAME=FILIN2, TYPE='OLD')
DO 30 I=1, NW
   READ (2, 15) D1, SIR(I)
30   READ (3, 15) D2, S2R(I)
CLOSE (UNIT=2)
CLOSE (UNIT=3)
OPEN (UNIT=1, NAME=FILOUT, TYPE='NEW')
SRPI=SORT(2*PI)
ENTER RANGE OF RADII, MEAN RAD. AND STD. DEV TO BE USED IN LNDF

TYPE 20
ACCEPT 21,RADSCL,RADLO,RADHI,RADBAR,RADSIG
DELRAD=(RADBAR)/20./RADSCL
RAD=RADLO-DELRAD
RMNL=ALOG(RADBAR)
SIGL=ALOG(RADSIG)
INRAD=0
TSTARE=RADBAR/RADSCL

COMPUTE RADII INCREMENT IN LNDF

(increment for radius is computed such that area under
LNDF function between radii equals a constant = TSTARE)
(this gives a distribution of radii whose density is log-normal)

AREA=0.0
RAD=RAD+DELRAD
IF (RAD,GT,RADHI) GO TO 110
AREA=AREA+DELRAD*(ALNDF(RAD-DELRAD,RMNL,SIGL)+ALNDF(RAD,
1,RMNL,SIGL))/2.
IF (AREA,LT,TSTARE) GO TO 45
INRAD=INRAD+1
TYPE 13,INRAD,RAD
RAD=RAD*1.0E-08
TAU=6.*RAD*2.*PI*2.9979E+10/(5.*VFERMI)

BEGIN OUTPUT TO LP: AND DISK FILE

PRINT 2
WRITE (1,2)
PRINT 26,VFERMI,WPLSQ,F,SUPER,RADLO,RADHI,INRAD,RADBAR,RADSIG
WRITE (1,26) VFERMI,WPLSQ,F,SUPER,RADLO,RADHI,INRAD,RADBAR,
1 RADSIG
PRINT 25
WRITE (1,25)

BEGIN LOOP OVER FREQUENCIES from WLO(cm-1) to WHI(cm-1)

DO 100 INC=1,NW
W=WLO+INC*WINC

CALCULATE EPS(metal) IN DRUDE MODEL

EMW=1.1-WPLSQ/(W*(W+PURIMA/TAU))
IF (SUPER,'N,'S') GO TO 60
C CONVERT TO SC USING PREVIOUSLY CALCULATED RATIOS FOR
C SIG1sc/SIG1 and SIG2sc/SIG1
C
EMW=SUP(S2R(INC)*S1R(INC)*EMW)
C
C COMPUTE ABSORPTION COEFFICIENT
C
60 AKPROP=2.*PI*RAD**2*(CSRT(EMW*UMET))
   IF (AIMAG(AKPROP).LT.0.0) AKPROP=-1.0*AKPROP
   IF (ABS(AKPROP).LT.1.E-30) GO TO 65
   POLAR=1./((AKPROP)**2+3.*CCOS(AKPROP))/(CSIN(AKPROP)
   *AKPROP)
   GO TO 66
65 POLAR=CMPLX(1.,0.)
66 UMS=1.+POLAR/(1.+POLAR/2.)
   EMGT=(EIN*(EMW**(2.*F1+1)+EIN*(2.-2.*F)))/(EIN**(2.+F)+
   EIN**(1.-F))
   UMG=(2.*EIN**(1.-F)*UMS)/(2+F)+(1.-2.*F)*UMS
   AKPROP=CSRT(EMGT*UMG)
   IF (AIMAG(AKPROP).LT.0.0) AKPROP=-1.0*AKPROP
   ABSORP(INC)=(4.*PI*WAIMAG(AKPROP))
   IF(INC50).EQ.(FLOAT(INC/50)) PAUSE 'Press <CR> when
   printer stops'
   WRITE (1,16) W,ABSORP(INC),EMW,EMGT,UMGT
100 PRINT 16,W,ABSORP(INC),EMW,EMGT,UMGT
   RAD=RAD*1.0E+08
   GO TO 42
C
C AVERAGE RESULTS FOR NUMBER OF RADIi USED
C
110 DO 150 I=1,NW
150 ABSORP(I)=ABSORP(I)/FLOAT(INRAD)
   CLOSE(UNIT=1)
C
C SET-UP FOR PLOTTING ON TT:
C
300 IARRAY(I)=ABSORP(I)/ABSORPNW*220
   CALL ERASE('A')
   CALL CURSOR(1,1)
   CALL SCROLL(1,3)
   CALL PLOT55(9,1,1)
   CALL PLOT55(10,1)
   CALL PLOT55(1,0,1)
   CALL PLOT55(2,0,1)
   CALL PLOT55(3,-512,IARRAY)
   PAUSE
CALL PLOTS5(2,3)
CALL SCROLL(1,24)
END

C LOG-NORMAL DISTRIBUTION FUNCTION

FUNCTION ALNDF(R,MNL,SIGL)
    ALNDF=EXP(-((ALOG(R)-MNL)**2/(2.*(SIGL**2)))//
               1/(2.506628*SIGL))
RETURN
END

C ROUTINE TO COMPUTE DIELECTRIC FUNCTION FOR SUPERCONDUCTORS

FUNCTION SUP(S2,S1,EMW)
    COMPLEX SUP,EMW
    E2MW=AIMAG(EMW)
    SUP=CMLX(1-S2*E2MW,S1*E2MW)
RETURN
END
PROGRAM TO COMPUTE FREQUENCY DEPENDENT CONDUCTIVITY FOR A SUPERCONDUCTOR USING MATTIS & BARDEEN RELATIONS -- INTEGRATION DONE BY GAUSSIAN QUADRATURE --

REAL INTGRD
TYPE 5

FORMAT(IH0,'File name for storage of results')
ACCEPT 6,FILOUT

FORMAT(44+)

DIMENSION FILOUT(4),AI(10),BI(10),SI(1000)
OPEN (UNIT=1,NAME=FILOUT,TYPE='NEW')

C

- ABSCISSAS AND WEIGHT FACTORS FOR 20-POINT GAUSSIAN INTEGRATION

C

DATA AI/.076526521,.22778585,.37370609,.510867,.63605368
1,.74633191,.8391697,.91223443,.96397193,.9931286/

DATA BI/.15275339,.14917299,.14209611,.13168864,.11819433
1,.10193012,.083276742,.062872048,.04080143,.01761407/

DATA SI/1000*O./

TYPE 7

FORMAT(IH0,'Frequency range to be calculated
1(lower,upper) and increm.')
ACCEPT 8,WLO,WHI,WINC

FORMAT(3F10.2)

FORMAT(/,IH$,'Input coherence (+1= destr., -1= cons(r.,
1 0= none ) ?')

FORMAT(I2)

TYPE 9

ACCEPT 11,ICOH

FORMAT(/,IH$,'Input real or imas. calc. (01= real, 02= imas
1, ) ?')

TYPE 12

ACCEPT 11,IRLIN

FORMAT(/,IH$,'Input full gap frequency (2Xdelta) ?'

ACCEPT 8,WGAP

WGAP2=WGAP/2.

CALL ERASE('A')

CALL CURSOR(11,15)

CALL LINE('D')

CALL CHAR('B','F')

CALL CURSOR(11,15)

TYPE 10
CALL CURSOR(12,15)
TYPE 10
CALL CHAR('N')
LSTOP=INT((WHI-WLO)/WINC)+1

10 FORMAT(1H,'INTEGRATING')
DO 50 L=1,LSTOP
W=(L-1)*WINC+WLO
X=W-2-W
Y=W+W
IF (IRLIM-1) 20,20,25
20 IF (W.LE.WGAP) Y=X
GO TO 35
25 Y=-Y
IF (W.GT.WGAP) X=-Y
35 S=(Y-X)/20.
T=X+S
R=0.

C
C - COMPUTE INTEGRAL OVER EACH SUBINTERVAL
C
DO 40 I=1,10
P=0.
IF (X.EQ.Y) GO TO 45
C
C - COMPUTE SUMMATION FACTOR FOR EACH SUBINTERVAL
C
DO 30 J=1,10
A=A1(J)
B=B1(J)
C=S*A+T
D=T-S*A
30 P=P+B*(INTEGRD(C,W)+INTEGRD(D,W))
R=R+P*S
40 T=TH2.*S
45 S1(L)=R/S
WRITE(1,70) W,S1(L)
50 PRINT 70,W,S1(L)
70 FORMAT(1H,F8.2,2X,612.5)
CLOSE(UNIT=1)
END
FUNCTION SUBPROGRAM TO PROVIDE INTEGRAND FOR
GAUSSIAN QUADRATURE INTEGRATING PROGRAM

FUNCTION INTGRD(X,W,GAP,ICOH)
REAL INTGRD
COH=FLOAT(ICOH)
WGAPX2=GAP*GAP
ARG1=GAPX2-X**2
ARG2=(X+W)**2-WGAPX2
INTGRD=ABS(X**2+COH*WGAPX2+W**2)/(SORT(ABS(ARG1))*
1SORT(ABS(ARG2)))
RETURN
END
LIST OF REFERENCES

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