Low Temperature Study of the Electronic Density of States of Antimony.

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BLEWER, Robert Sewall, 1939–
LOW TEMPERATURE STUDY OF THE ELECTRONIC
DENSITY OF STATES OF ANTIMONY.

Louisiana State University and Agricultural and
Mechanical College, Ph.D., 1967
Physics, solid state

University Microfilms, Inc., Ann Arbor, Michigan
LOW TEMPERATURE STUDY
OF THE
ELECTRONIC DENSITY OF STATES OF ANTIMONY

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in
The Department of Physics and Astronomy

by
Robert Sewall Blewer
M.S., Louisiana State University, 1965
January, 1967
ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to
Dr. Nadim H. Zebouni for his active assistance and keen interest
in all phases of this research and for his guidance as research
director. Warmest thanks and gratitude are also due Dr. Claude
G. Grenier for enlightening discussions and the generous gift of
his understanding during various phases of the experiment. The
author is also indebted to Dr. Joseph M. Reynolds for his effective
supervision of the overall research effort in this laboratory which
has made this work possible.

The author gratefully acknowledges the skillful help of
Charles Burlo in various phases of the research, the assistance of
Mr. D. VanDerBaaren in taking and analyzing part of the data. In
that regard, the assistance of Robert E. Hamburg, Syed Wasim, S.
C. Schiff, Lawrence Rouse, and Raymond F. Folse is also acknowledged.
Charles R. Crosby is due thanks for his help with computer analysis
of the data. The electronic skills of Leslie Edelen, and the labors
of Phil Granata and L. M. Overman are also acknowledged. Thanks
are due machinists Edward T. Keel and Mr. Kirby and glassblower
Morris Dunlap for constant assistance with the construction and
maintenance of the equipment.

The generous help of Dr. B. B. Townsend, Director of L.S.U.
Computer Center, and E. L. Morton is acknowledged and appreciated.
All computer work was done entirely through the use of the L.S.U.
Computer Center.

Grateful acknowledgement is made to Pat Mills for typing and
other work on the manuscript.

Special thanks are due my wife, Martha, in taking part of the
data, and for her constant help and encouragement over this arduous
course.

Not forgotten and hereby belatedly acknowledged is the complete
and selfless help rendered during the early stages of research by our
late friend, Ambale Venkataram.
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ABSTRACT

The determination of the electronic density of states in energy $Z_{E_F}^e$ of antimony has been a controversial subject, different experimental methods yielding different results. Two independent determinations were conducted in this study through specific heat measurements and transport effects measurements. The two samples were taken from a common zone-refined bar. Use of a He$^3$ refrigerator, especially built for this work, allowed the temperature range in both types of measurements to be lowered to 0.37°K, extending the range of any previously published similar work. As a consequence good agreement is found between results from the two types of measurements, viz. $Z_{E_F}^e(\text{Sp.H}) = (1.011 \pm 0.046) \times 10^{33} \text{erg}^{-1} \text{cm}^{-3}$, $Z_{E_F}^e(\text{Transport}) = (1.069 \pm 0.075) \times 10^{33} \text{erg}^{-1} \text{cm}^{-3}$. Complete determination is also obtained of the electric quadrupole $C_Q$ electronic $C_e$ and lattice $C$ contributions to the specific heat of antimony. $C_Q = \frac{0.00197 \pm 0.00023}{T^2}$, $C_e = (0.11654 \pm 0.00644)T$, $C_L = (0.2110 \pm 0.0053)T^3$, in millijoules mole$^{-1}$deg$^{-1}$. The lattice thermal conductivity is determined down to temperatures lower than previously published. Perfect $T^2$ dependence is found below 1°K, confirming the predominance of phonon-electron N-type scattering. Anomalous temperature dependences of previous investigations are clarified. Comparison with theory reveals an additive contribution to the conductivity below 1°K. This is tentatively explained in terms of the uncoupling of the transverse and longitudinal lattice waves below that temperature.
INTRODUCTION

In the experimental verification of the theory of solids, the semimetals have received much attention. Included in this group are the elements bismuth, antimony, and arsenic, which are conducting at absolute zero with the carriers consisting of equal, small numbers of electrons and holes. Thus in addition to the purely electronic effects normally measured in metals, thermal effects involving electronic interaction with the lattice can be conveniently studied in the three elements comprising this group and the results used to verify and explain the basic theory of metals.

Antimony was the semimetal chosen for the present study. The objectives of the experiments performed were twofold: to determine by two separate independent methods the electronic density of states in energy of this semimetal in the temperature range between 2.5°K and 0.4°K, and, secondly, to measure the lattice thermal conductivity in the same low temperature range. A persistent discrepancy between predicted and measured values for the density of states for all semimetals, as well as recent results indicating a striking anomaly in the temperature dependence of the lattice thermal conductivity of antimony made this study particularly desirable.

Specifically, in the general study of the transport properties of antimony, Long et al. observed in a very pure ($\rho_{300K}/\rho_{4.2K} = 3600$) single crystal of antimony, that the lattice thermal conductivity in the temperature range between 1.6°K and 4.2°K was proportional to the 4.8th power of the absolute temperature.
Although this temperature dependence is anomalous the ratio of the electrical intrinsic conductivity to the thermal lattice conductivity was found to be in excellent agreement with theory. This led to the tentative conclusion that the lattice resistance in the crystal was due to electron-phonon scattering in the temperature range investigated. At very low temperature this would predict a lattice thermal conductivity proportional to the square of the temperature. It was one of the purposes of this work to check the validity of this prediction.

It was also determined in the work of Long et al. that the density of states obtained from the asymptotic behavior of the Nernst-Ettinghausen coefficient \( e^{1/2} \) was large and temperature dependent; this result was rather successfully explained in terms of an added component to the density of states proportional to the square of the temperature and due to the phonon drag effect. But because of this added effect, the extrapolated value of \( \Sigma Z_i^{\text{eff}} \) at \( T = 0^\circ \text{K} \) was somewhat uncertain, and appeared to be higher than predicted by free electron theory. This high density of states found in antimony, as well as similar results reported in other semimetals, made desirable an extension of these measurements to lower temperatures in order to reduce the contribution due to phonon drag and to improve the accuracy of the extrapolation to \( 0^\circ \text{K} \).

As an independent check, it was decided to also measure the density of states of antimony by an entirely different technique. The method chosen was the measurement of the electronic component
of the specific heat which gives a direct indication of the density of states. In addition to the intended information, this part of the experiment yielded valuable information about other contributions to the specific heat of antimony in a temperature range lower than had been previously reported.

Definitions of the basic defining equations for the kinetic transport coefficients, and a brief outline of experimental methods follow these introductory paragraphs. The theoretical predictions and the experimental results with their discussion follow in three successive sections. Section III deals with the results of the lattice thermal conductivity measurements. Section IV deals with the density of states results as deduced from the measured pertinent transport coefficients. In Section V the specific heat determination of the density of states is given and discussed, and its bearing on the related results from transport measurements are given. Section VI summarizes the conclusions of the experiments. The full range of experimental details is given in an appendix since both the attainment of working temperatures below 10K and the measurement of specific heat at low temperature have been performed for the first time in this laboratory.
I. PHENOMENOLOGICAL DEFINITIONS OF THE TRANSPORT EFFECTS

The transport effects can be described in irreversible thermodynamics as processes involving a "force" parameter, i.e., an "affinity", which drives the process, and an additional parameter, the "flux", to describe the response to this force. In transport measurements the electrical and thermal current densities, $J$ and $W^*$ respectively, (the "fluxes"), are expressed as linear combinations of the electric field $E^*$ and the negative of the temperature gradient $G$ (the affinities), by the following equations

$$J = \sigma E^* - \epsilon^* G$$

$$W^* = -\pi^* E^* + \lambda^* G$$

(1)

The asterisk notation on $E^*$ and $W^*$ is used to indicate that the internal quantities have been modified for convenience by a term involving the chemical potential $\zeta$ so as to represent measured quantities. The kinetic coefficients defined by Eq. (1) are the quantities calculated from formal transport theories, and are called, respectively, the electrical conductivity tensor $\sigma$, the thermal conductivity tensor $\lambda^*$, the thermoelectric power $\epsilon^*$, and the Peltier tensor $\pi^*$. The transport measurements were made with the magnetic field parallel to the trigonal axis (see Fig. 1 for orientation of the Cartesian axes). Threefold symmetry perpendicular to the plane in which the effects were measured implies that the kinetic equations
for two dimensional isotropic media are applicable. Then the coefficients defined by Eq. (1) are each 2 X 2 tensors, and by symmetry, each is isomorphic to the complex numbers, giving a convenient way to compute and represent the transport effects.

Because the physical conditions needed to measure the kinetic coefficients directly are not readily attainable in the laboratory, it is convenient to express other relations between $J$, $W$, $E$, and $G$ as follows:

$$E^\star_{\text{iso}} = \hat{\rho}J + \hat{c}G \quad (2)$$

$$W^\star_{\text{iso}} = -\hat{\pi}J + \hat{\lambda}G$$

The absence of primes on these coefficients indicates the "isothermal" condition, $G_{12} = 0$. The isothermal electrical resistivity tensor $\hat{\rho}$ is simply related to the kinetic electrical conductivity tensor $\hat{\sigma}$ of Eq. (1) by the relation $\hat{\rho}^{-1} = \hat{\sigma}$. The other coefficients defined above are called the absolute thermoelectric tensor $\hat{c}$, the isothermal Peltier tensor $\hat{\pi}$ and the thermal conductivity tensor $\hat{\lambda}$.

For measurements of thermoelectric and thermomagnetic phenomena, the elements of the tensors defined by the following relations are determined experimentally.

$$E^\star_{\text{adi}} = \hat{\rho}^\prime J + \hat{c}'W^\star \quad (3)$$

$$G^\ast = \hat{\pi}^\prime J + \hat{\gamma}W^\star$$

The primed coefficients above indicate the "adiabatic" condition $W^\star_{12} = 0$. The coefficients of this form are called the adiabatic
electrical resistivity tensor $\hat{\rho}'$, thermoelectric tensor $\hat{e}'$, the
Peltier tensor $\hat{\pi}$, and the thermal resistivity tensor $\hat{\gamma}$.

The kinetic coefficients are obtained from these experimental
coefficients through the relations $\hat{\lambda}'' = \hat{\gamma}^{-1}(1 + \hat{e}'\hat{\rho}-\hat{\gamma}-1\hat{T})$ and
$\hat{\pi}'' = \hat{e}'\hat{\gamma}^{-1}\hat{T} = \hat{\sigma}\hat{\gamma}^{-1}\hat{T}$. In practice, the term $\hat{e}'\hat{\rho}-\hat{\gamma}-1\hat{T} = \hat{e}'\hat{\pi}''$
is usually negligible compared to unity and thus $\hat{\lambda}'' \approx \hat{\gamma}^{-1} = \hat{\lambda}$.16,17

Foundations and applications of Eqs. (1), (2), and (3) have been
explored in detail18,19; further discussion concerning their use in
the present context can be found in articles by Grenier, et al.20,21
II. EXPERIMENTAL SUMMARY

General

The magnet, flask system, and measuring circuits are described elsewhere\(^\text{22,23}\) except as noted below, and will not be described here. An important innovation however was the design, construction, and installation of a "Helium 3" refrigerator capable of producing a temperature environment between 0.4°K and 1.2°K. An electrical temperature regulator was installed as an integral part of the refrigerator system to assure the required temperature stability (less than 0.001°K fluctuation over a twenty minute period). Techniques involved in using this type refrigeration system were evolved slowly, and since they require detailed exposition, are included in an appendix, together with a more extensive account of all experimental details involved in this experiment.

Transport Measurements

The sample used in this measurement was a 99.9999\(^\circ\)/\(^\circ\) pure antimony\(^\text{24}\) single crystal used by Long in his transport experiments. It was decided to use the same sample in this experiment so that the results obtained in the lower temperature range investigated could be directly compared to those of Long taken at higher temperatures. The crystal was mounted so that the magnetic field lay along the trigonal axis, to take advantage of isotropy in the basal plane. Dimensions were 20 X 4.6 X 2 mm with the 4.6 mm width along a binary axis (see Fig. 1). The value of the resistivity ratio of the crystal,
Fig. 1
$\rho_{300}/\rho_{1.2}^0$ as measured by Long et al. was 9500; the residual resistivity $\rho_0$ had a value of $4 \times 10^{-9} \, \Omega \, \text{cm}$. The length of the crystal was mounted vertically and soldered to the copper sample holder with Woods metal. Undesirable superconducting effects of the solders used were not a consideration because all measurements were made at 12.7 kilogauss.

Since the sample holder housed the $\text{He}^3$ evaporator in its interior, the sample holder served as the heat sink for the sample. Heat was supplied by a 111 $\Omega$ non-inductive constantan wire (No. 38) heater wound on a No. 16 copper wire which was soldered to the base of the sample (see Fig. 1). Thermal measurements were taken with the crystal thermally isolated by a vacuum in range of $10^{-10} \, \text{mm Hg}$ obtained by carefully flushing the sample chamber at room temperatures with helium-free nitrogen gas, pumping it to approximately $10^{-3} \, \text{mm Hg}$, and sealing off the space. When liquid helium was transferred before the run, a high vacuum was produced by the cryopumping effect.

Thermal and electrical probes were connected as shown in Fig. 1. For the low range of temperatures investigated it was found that 10 $\Omega$, 1/10 watt Allen Bradley resistors had the proper sensitivity. At temperatures below 0.9$^0\text{K}$ it was found necessary to limit the thermometer current to 0.2 microamperes if self-heating effects in the thermometers were to be avoided. Under these conditions, the thermometers were found to obey very accurately the relation between their resistance $R$ and the vapor pressure of the helium-3 liquid, $P$ given by

$$\log R = a + \sum \frac{b_n}{n} \left( \log P \right)^n.$$  

Field orientation of the crystal was accomplished by finding the resistance minimum of a zinc crystal $Z$, mounted parallel to the basal plane of the antimony (see Fig. 1).
For the measurement of the isothermal longitudinal electrical resistivity $\rho_{11}$, a current of 1.2 mA was used. Heat currents for the thermomagnetic phenomena ranged from 0.5 $\mu$W at 0.44°K to 150 $\mu$W at 2.3°K, taking care to keep the temperature gradient sufficiently small ($< 0.1°K/cm$) to apply linear approximations in the computations.

Heat Capacity Measurements

The sample for the heat capacity measurements was a 142.429 gram bar of antimony cut from the same parent bar from which the crystal was obtained for the transport measurements. The sample was soldered to the base of a platform suspended from the evaporator of the He$^3$ refrigerator by 3, 3 mm diameter graphite rods 5 cm long (see Fig. 2). A 0.001 inch diameter 99.995°/o pure lead wire drawn by the Wollaston process was used in conjunction with the magnetic field as a superconducting heat switch.

Measurements were made by thermally isolating the sample when it had been cooled to a temperature of ~ 0.37°K and then supplying well determined amounts of heat for accurately known periods of time, taking care not to change the temperature of the sample by more than 7°/o with each heat pulse. The electronic timer used could be read accurately to microseconds and was arranged in the heater circuit so as to be automatically activated when the heater was started (see Fig. 12). The temperature of the sample was recorded as a function of time on a Brown stripchart recorder.

The technique of accounting for the heat capacity of the addenda was as follows. A separate run was made in which most of the sample
Fig. 2
had been cut off with a spark cutter, and only that portion which
was wetted with solder was left as part of the addenda. The measure­
ment of heat capacity in this run was subtracted from that taken with
the entire bar attached, and this difference taken as the heat
capacity due to the amount (126.354 grams) of pure antimony removed.35

The heat pulses applied ranged in magnitude from 0.5 microwatts
at the lowest temperatures to 6 microwatts near 1ºK. Heating periods
ranged from 2 seconds to 6 seconds depending on the criterion of
less than 7º temperature rise per heat pulse stated above. The
heat leak from extraneous sources to the sample was determined to
be about 20 ergs per minute. Complete details on measurement
techniques and data reduction methods are given in the Appendix.
III. LATTICE THERMAL CONDUCTIVITY

A. Theory

In the determination of the electronic density of states through the kinetic coefficients, it is necessary to measure, among other factors, the adiabatic thermal conductivity at fields of about 12 kilogauss.\textsuperscript{36} It is of interest to compare the results of this measurement to theoretical predictions, particularly since the electronic properties of antimony have interesting features not found in metals in general.

The small number of electrons in Bi and Sb allows the conduction of heat by phonons to be easily observed. Any electronic heat conduction can be separated out by the application of a magnetic field. But even without this, the lattice conduction is the main part of the whole thermal conductivity\textsuperscript{37} in the case of bismuth.\textsuperscript{38} In antimony, on the other hand, the electron density is larger than in bismuth and at very low temperatures this has made it possible, in this experiment, to observe a phonon conductivity limited mainly by scattering by the conduction electrons.

The thermal conductivity can be expressed as the sum of a lattice and an electronic contribution:

\[ \lambda'' = \lambda''_e + \lambda''_g \] \hspace{1cm} (4)

In presence of a magnetic field the electronic term $\lambda''_e$ is of the form $\sim H^{-\eta}$ and the lattice term is approximately constant at a given temperature. It was experimentally established by Long\textsuperscript{39}
that at reasonably high magnetic fields (5 kG), the thermal resistivity $\gamma_{11}$ approaches an asymptotic value, and $\gamma_{12} \rightarrow 0$, so that

$$\lambda'' \approx \lambda = \frac{1}{\gamma} = \frac{1}{(\gamma_{11}^* + i \gamma_{12}^*)} \rightarrow \text{constant} \quad (5)$$

which is an indication that the field-dependent electronic component, $\lambda''_{e}$, of the thermal conductivity has been "quenched" by the magnetic field. Thus at moderate fields, it is possible to observe quite easily almost pure lattice conduction of heat in a metal, an opportunity which is unique to the semimetals.

The thermally resistive effects of possible importance in limiting lattice thermal conductivity can be expressed as a sum of different types of scattering processes.

$$\frac{1}{\lambda} = \gamma_u + \gamma_i + \gamma_l + \gamma_B + \gamma_e \quad (6)$$

where $\gamma_u$ is the thermal resistance due to phonon-phonon Umklapp processes, $\gamma_i$ to imperfections, $\gamma_l$ to isotope "impurities", $\gamma_B$ to boundary scattering, and $\gamma_e$ to phonon-electron scattering.

(Notice that subscripts on resistivities refer to scattering processes, while subscripts on the conductivity symbol refers to the name of the carrier.)

The first of these effects, phonon-phonon Umklapp processes, tend to be "frozen-out" when temperatures well below the Debye temperature are reached: The energy $\hbar \nu''$ of a phonon created in three phonon Umklapp processes $\vec{q}'' = \vec{q} + \vec{q}' - \vec{g}$ must be greater than $\sim k \theta/2\zeta$; the sum of the energies of the phonons which have combined
in the scattering, $h\nu + h\nu'$ must obey the same conditions; the total number of such processes should be proportional to the product of the occupation numbers of these two modes, and at low temperatures should be of the form

$$n_q^- n_{q'}^- \propto \exp\left(-\frac{h\nu}{kT}\right) \exp\left(-\frac{h\nu'}{kT}\right)$$

$$n_q^- n_{q'}^- \propto \exp\left(-\frac{h\nu + h\nu'}{kT}\right)$$

$$n_q^- n_{q'}^- < \exp\left(-\frac{\theta}{2T}\right)$$

This shows that the rate at which Umklapp processes occur becomes negligible at low temperatures, and these U-processes are thus not available to provide a resistive mechanism on the heat current. They are negligible in the analysis of the thermal conductivity measured in this experiment.

Imperfection scattering is also not important in this case because the sample was a single crystal. Scattering by impurities is generally unimportant at very low temperatures because the lengthening of the lattice waves makes point defect scattering of the phonons negligible. However, isotope scattering may be a real factor in the case of antimony because this semimetal is composed of nearly equal portions of two isotopes, Sb $^{121}$ and Sb $^{123}$, so that the proportion of "impurity" is much larger than that of any foreign chemical impurity. If isotope scattering was a factor in this experiment, $\frac{1}{\lambda_g}$ should contain a component proportional to $T$. This will be discussed with the results.
Thermal resistance due to boundary scattering should occur only at very low temperatures and then only if scattering from other causes is so small that the phonon mean free path $\Lambda_q$ becomes of the same order of magnitude as the dimensions of the sample. Then the mean free path of the phonons is limited only by the boundaries of the sample. If this situation occurs, the kinetic formula for the thermal conductivity of an assembly of phonons \(^{42}\)

$$\lambda_g = \frac{1}{3} C_g \bar{v} \Lambda_q$$

(7)

reduces to a $T^3$ dependence since

- lattice specific heat, $C_g \propto T^3$
- velocity of sound, $\bar{v} \propto$ constant
- phonon mean free path, $\Lambda_q \propto$ constant $\propto$ smallest dimension of sample.

Thus $\gamma_B \propto T^{-3}$. Order of magnitude calculations for $\Lambda_g$ on the basis of kinetic formula gives $\lambda_g \sim 2 \times 10^{-3} T^{-1} \text{cm}$, much smaller than the least dimension of the crystal, indicating that boundary scattering did not occur in this sample at temperatures below 10K.

The remaining resistive mechanism, and in this experiment probably the most important, is phonon-electron scattering. The generally accepted Makinson formula \(^{43}\) gives the temperature dependence of the thermal conductivity in the low temperature limit where electron-phonon $N$-processes would be expected to dominate over $U$-processes.

$$\frac{1}{\gamma_e} = \frac{27}{4\pi^2 n_a^2} \left( \frac{I}{\theta} \right)^2 \left[ \frac{\sinh(\theta/T)}{\theta/T} \right]^2 - \frac{3.67}{6} \left( \frac{I}{\theta} \right)^2 \lambda_{\text{el}} \lambda_{\text{el}}$$

(8)
where \( \lambda_{e_{\theta}}^{\|} \) is the electronic component of thermal conductivity under the assumption \( \frac{\theta}{T} \rightarrow \infty \) (\( \lambda_{e_{\theta}}^{\|} \) constant), and \( n_a \) is the number of carriers per atom. The \( J \) integrals are Debye integrals\(^{44}\) of the form

\[
J_n(x) = \int_0^x \frac{z^{n-1}}{(e^{z-1})} dz, \quad x = \frac{\theta}{T}
\]

\( J_n(x) \sim \frac{1}{n-1} x^{n-1} \), \( x \rightarrow 0 \)

\( J_n(x) \sim n! \sum_{r=1}^{n} \frac{1}{r^n} \), \( x \rightarrow \infty \)

The temperature dependence of the lattice conductivity of Sb has been a matter of conjecture since the measurements of Rosenberg,\(^{45}\) White and Woods,\(^{46}\) and Long et al.\(^{47}\) These last authors found anomalous temperature dependences for both the ideal electrical conductivity \( \sigma_i \) (\( \propto T^{-2.2} \)) and the lattice thermal conductivity (\( \propto T^{4.8} \)). Their analysis however pointed out that the ratio of the conductivities \( \lambda_{g}^{\|}/\sigma_i \) was in excellent agreement with the \( T \)\(^7\) law derived by Ziman,\(^{48}\) for the case of phonon-electron scattering,

\[
\lambda_{g}^{\|}/\sigma_i \geq \frac{1}{n_a^2} \left( \frac{k}{e} \right)^2 \left( \frac{\alpha}{3Nk} \right)^2 T, \quad n_a = \text{carriers/atom}
\]

where the inequality applies when U-processes are present. If all the scattering is N-type and the Debye approximation for the specific heat \( C \) is used, this equation becomes

\[
\lambda_{g}^{\|}/\sigma_i = \frac{48\pi^6}{25} \frac{L}{n_a^2} \left( \frac{\theta}{T} \right)^7, \quad L = \text{Lorentz Number}
\]
Long et al. found tentative agreement for $\theta = 178^\circ K$ and $n_a = 2.4 \times 10^{-3}$ carriers/atom. As a consequence it was concluded that the only scattering of any consequence was due to an electron-phonon N-process. On the basis of this assumption, the apparently anomalous temperature dependence of $\sigma_i$ was made plausible by the introduction of an effective Debye temperature for scattering of phonons by electrons: The usual criterion in a metal where an electron-phonon N-process occurs is that the limiting value of the scattered phonon wave vector $q$ be taken as $q_d$, the Debye sphere radius. However, if $2k_F$, the diameter of the Fermi sphere, is smaller than $q_d$, the limiting value of $q$ should be taken as $2k_F$ instead of $q_d$, thus introducing an effective Debye temperature

$$\theta^* = \left( \frac{2k_F}{q_d} \right) \theta \quad (12)$$

Long et al. found good agreement with their experimental value of $\sigma_i$ for $\theta^* \sim 10^\circ K$ to $15^\circ K$.

Using these same premises we attempt to fit our thermal conductivity data by the formula

$$\lambda_g = \frac{4\pi^6}{25} \frac{L}{n_a} \frac{\theta}{(r^2)} \sigma_i \quad (13)$$

or, using

$$\sigma_i = \frac{1}{4} \left( \frac{T}{\theta} \right)^{-5} \left( \frac{\theta}{T} \right)^{-1} \sigma_\theta \quad (14)$$

Eq. (13) becomes

$$\lambda_g = 27 \times 10^{-3} \pi^6 \left( \frac{T}{\theta} \right)^2 \left[ \frac{\theta}{T} \right]^{-1} \sigma_\theta$$

$$= 27 \times 10^{-3} \pi^6 \left( \frac{T}{\theta} \right)^2 \frac{\theta}{T} \left[ \frac{\theta}{T} \right]^{-1} \sigma_\theta$$
Since for \( T \ll \theta^* \), \( J_5 \rightarrow 5! \sum \frac{1}{n^5} = 124.4 \), one expects \( \lambda \propto T^2 \) at very low temperatures, e.g., those attainable with a He\(^3\) refrigerator (\( 0.3^\circ K < T < 1^\circ K \)), but above 1\(^\circ\)K one should expect the temperature dependence to be determined by the behavior of \( J_5 (\frac{\theta^*}{T})^4 T^2 \).

**Effect of Uncoupling of Transverse and Longitudinal Modes of Lattice Vibrations**

The details of the theory\(^\text{50}\) of the scattering of phonons by electrons, in the context of lattice thermal conduction, depend upon the coupling between the conduction electrons and the longitudinal and transverse phonons.

If one defines an electron-phonon interaction parameter \( C(q) \), one can then consider 3 possibilities:

- **a)** \( C_L^2 = C_T^2 \): longitudinal and transverse phonons interact equally strongly with the conduction electrons. This is the assumption made by Makinson.\(^\text{51}\)

- **b)** \( C_L^2 > C_T^2 \) (in particular \( C_T^2 = 0 \)): the transverse waves do not interact as strongly (or not at all) with the conduction electrons and are tightly coupled to the longitudinal waves.

In this case the contribution to the thermal conductivity from the transverse phonons will not be higher than that given by Makinson's coupling model, because the tight coupling has for effect to equalize the mean free paths of the phonons of the same frequency but different polarization.

- **c)** \( C_L^2 > C_T^2 \): the transverse waves do not interact as strongly with the conduction electrons and are only loosely coupled to the...
longitudinal waves.

In this case there arises an additional component of conductivity, which will be considered in the discussion.

B. Results and Discussion

The results of the thermal conductivity measurements are shown in Figs. 3, 4 and 5. Figure 3 displays the temperature dependency of the lattice thermal conductivity on a logarithmic plot. It can be seen that below $T = 1.4^\circ K$, a perfect $T^2$ dependence prevails down to the lowest temperature attained. This confirms the assumption made by Long et al. of a lattice conductivity limited by predominant N-type electron scattering. In the region above $T = 1.6^\circ K$, our results confirm the local $T^{4.8}$ dependence as found by Long et al. It is to be noted that Woods and White in this same temperature region find a $T^{3.6}$. In Fig. 4 a logarithmic plot of $\lambda / T^2$ versus $T$ is presented together with the temperature dependence expected from the $T^2[\frac{\theta (e)}{T}]^{-1}$ (solid curve). This solid curve is obtained by assuming a good fit of the experimental points in the upper temperature region, and it corresponds to a value of the reduced Debye temperature $\theta^\ast = 11^\circ K$. This value is in reasonable agreement with that obtained by Long et al. from consideration of their ideal electrical conductivity ($\theta^\ast \sim 10-15^\circ K$).

The most interesting feature seen in Fig. 4 is an additive contribution to the conductivity in the lower temperature region $T < 1.3^\circ K$. Additive conductivity is seen from the plot to have an approximate $T^2$ dependence. If we write $\lambda_{\text{exp}} = \lambda_{\text{th}}(1 + \alpha)$ we find from Fig. 4
$\lambda \left(10^{-3} \text{ Watts cm}^{-1} \text{°K}^{-1}\right)$

Diagram showing a relation between $T$ (°K) and $\lambda$. The graph includes a linear trend line and data points represented by different shapes.
Fig. 4
Fig. 5
that \( \frac{\lambda_{\text{exp}}}{\lambda_{\text{th}}} = \frac{2.9}{2.2} = 1.31 \) or \( \alpha = 0.31 \), i.e., a 31\% increase. There are two mechanisms that can contribute an additive component to the conductivity at low temperatures:

1) Pippard's Phenomenon. Pippard\textsuperscript{54,55} has suggested that the mean free path \( \Lambda_p \) of a phonon of wave number \( q \) scattered by an electron should depend on the electronic mean free path \( \Lambda_e \). The Pippard theory was initially developed to describe ultrasonic attenuation in metals and leads to expression for the attenuation coefficients of longitudinal and transverse sound waves as functions of \( q\Lambda_e \). The reciprocal of the attenuation coefficient is interpreted as being equal to the phonon mean free path \( \Lambda_p \) and yields the expression

\[
\Lambda_p = \frac{Dv_s\Lambda_e}{Nm v_F} \left[ \frac{1/3(q\Lambda_e)^2\tan^{-1}(q\Lambda_e)}{(q\Lambda_e) - \tan^{-1}(q\Lambda_e)} - 1 \right]
\]

(15)

where \( D \) is the density of the metal, \( v_s \) is the velocity of sound, \( N \) is the number of conduction electrons per unit volume, \( m \) is the electronic mass, and \( v_F \) is the Fermi velocity. If \( q\Lambda_e > 1 \), we may expand the above expression in a series in \( (q\Lambda_e)^{-1} \) and write for the phonon mean free path

\[
\Lambda_p = \Lambda_p^\infty \{ 1 + \frac{8}{\pi} - \frac{\pi}{2} \frac{1}{q\Lambda_e} + \ldots \}
\]

(16)

where \( \Lambda_p^\infty \), taken as the limit of Eq. (15) as \( q\Lambda_e \to \infty \), is equal to

\[
\Lambda_p^\infty = \lim_{(q\Lambda_e) \to \infty} \Lambda_p = \frac{6Dv_s}{\pi N m v_F q}
\]

(17)
The lattice contribution to the thermal conductivity is given in general by the kinetic equation \( \lambda_g = \frac{1}{3} C_g v_A \), where \( C_g \) is the Debye specific heat, proportional to \( T^3 \) at low temperatures. Taking \( q = q_c \), the mean wave number of the phonons present at temperature \( T \), (for \( T \approx 0.5^\circ K \)) \( q = \frac{2kT}{h_\nu} \approx 10^5 \text{ cm}^{-1} \) we find, after substituting Eq. (16) into the kinetic equation,

\[
\lambda_g \propto T^2(1 + \frac{A}{T} + \ldots) \quad \text{where} \quad A \approx \frac{h\nu}{3k\Lambda_e}.
\]  

(18)

Order of magnitude calculations based on the residual resistivity of the sample indicate that \( \Lambda_e \approx 10^{-2} \text{ cm} \), and taking \( v_s \approx 3 \times 10^5 \text{ cm/sec} \), then \( A \approx 2 \times 10^{-4} \text{ K} \). Thus at \( T = 0.5^\circ K \), the added lattice conductivity expected from the Pippard effect amounts to a 0.01\% increase and is much too small to explain the 31\% excess conductivity observed in Fig. 4.

This was to be expected since the electronic mean free path is too long in antimony in relation to the average phonon wave number at \( T = 0.5^\circ K \) to expect the Pippard phenomenon to be observed.

2) Effect of Uncoupling of the Different Modes of Lattice Waves. If one assumes that the longitudinal phonons interact more strongly with the electron scatterers than the transverse phonons do, one has to consider the effect of the coupling between the two systems of phonons.

A tight coupling between the polarization branches has for effect to equalize their mean free path. As the temperature is lowered it can be expected that a transition from tight to loose coupling
takes place. Under these circumstances, $\Lambda_T$ can now become larger than $\Lambda_L$. This allows the system of transversely polarized phonons to contribute an additional term to the conductivity and since in phonon-electron scattering, the mean free path is inversely proportional to $T$, this added contribution, namely $2v_T C_T \Lambda_T$, will have a $T^2$ dependence ($C_T \propto T^3$).

**Isotope Scattering**

We examine briefly the effect of isotope scattering. This is certainly present in antimony since there are two isotopes $\text{Sb}^{121}$ and $\text{Sb}^{123}$ and their natural abundance ($57.25\% \text{Sb}^{121}$ and $42.75\% \text{Sb}^{123}$) is comparable. If the thermal resistance associated with phonon-electron scattering and isotope scattering were composed additively of the individual resistivities $\frac{1}{\Lambda} = AT^{-2} + BT$. This obviously would lead to the presence of a minimum in the resistivity for $T_{\text{min}} = \frac{3}{2B}$. The corresponding maximum in the conductivity might be associated with that observed by workers Woods and White at a temperature around $90\text{K}$.\textsuperscript{57}

On the other hand, the isotope resistance $BT$ would rapidly become negligible below $T_{\text{min}}$. It is therefore concluded that it does not contribute significantly in the temperature range covered in the present work.
IV. DENSITY OF STATES AND THE TRANSPORT COEFFICIENTS

A. Relation Between the Density of States and Certain Transport Effects

The electronic density of states in energy is related to the components of the kinetic thermoelectric tensor, $e''$. Integration of the Boltzmann transport equation by means of a relaxation time gives the following relationship between the density of states and the components of $e''$ generalized to a multiband model:

\[
e''_{11} = -\frac{1}{3}\pi^2 k^2 c T \sum_i \frac{a_i f(\alpha) H_i Z_i}{H^2 + [f(\alpha) H_i]^2}
\]

\[
e''_{12} = -\frac{1}{3}\pi^2 k^2 c T H \sum_i \frac{Z_i}{H^2 + [f(\alpha) H_i]^2}
\]

The notation is as follows (cgs gaussian units):

- $k$: Boltzmann constant
- $Z_i$: density of states of the $i$th band
- $H$: applied magnetic field
- $a_i$: orbital ellipticity parameter ($a_i = 1$ for circular orbits)
- $\alpha$: scattering efficiency indicating the degree of elastic scattering of phonons ($\alpha = 1$ for perfectly elastic scattering)
- $f(\alpha)$: an undetermined empirical function of $\alpha$
- $H_i$: saturation field defined by the equation
  \[
  H_i = \frac{m_i^* c}{e \tau_i}
  \]
  $m_i^*$: effective mass of carriers in the $i$th band
  $e$: electronic charge
  $\tau_i$: relaxation time of carriers in the $i$th band
The use of a relaxation time in the above formulation is justified in principle only if the scattering is of the static point defect type (elastic), and if $\omega t < 1$ where $\omega = eH/m^*c$, the cyclotron frequency. However, it has been previously noted that the requirement $\omega < 1$ is not binding. \(^6^2\)

The above equation predicts that $\epsilon''_{12}$ under high field asymptotic conditions ($H \gg H_1$) will approach a limiting value of

$$\epsilon''_{12} = -\frac{\Lambda^2k^2eT\Sigma Z_i}{H}$$  \hspace{1cm} (21)

directly proportional to the sum of the density of states.

Thus the determination of $\epsilon''_{12}$ gives in principle a measure of the density of electronic states for the $i$ bands of the metal. $H_1$ for both holes and electrons has been shown \(^6^3\) to be smaller than 500 Gauss in the case of antimony, so that our measurements are unambiguously in the asymptotic condition and Eq. (21) above holds.

As was mentioned in the previous section, the kinetic coefficients are not measured directly in experiments but are determined through the coefficients derived in Eqs. (2) and (3). As pointed out on page 51, the expression for $\epsilon''_{12}$ in terms of the measured coefficients can be found as follows

$$\hat{\epsilon}'' = \epsilon''_{11} + i\epsilon''_{12} = (\epsilon'_{11} + i\epsilon'_{12})(\sigma'_{11} + i\sigma'_{12})(\lambda'_{11} + i\lambda'_{12}) \approx \epsilon'\gamma^{-\Lambda - 1}$$

So that

$$\epsilon''_{12} = \sigma'_{11}(\lambda'_{11} + \lambda'_{12}) + \sigma'_{12}(\lambda'_{11} - \lambda'_{12}) + \sigma_{12}\epsilon_{cn}$$
where the last term is the thermoelectric power of the constantan leads.

\[
\varepsilon_{12}'' = \sigma_{11} \lambda_{11} \left[ \varepsilon_{11}' \left( \frac{\lambda_{12}}{\lambda_{11}} \right) + \sigma_{12} \sigma_{11} \varepsilon_{12}' \left( \frac{\lambda_{12}}{\lambda_{11}} \right) + \frac{\sigma_{12}}{\lambda_{11}} \varepsilon_{cn} \right]
\]

Now in the limit \( H \gg H_i \), for \( T < 1.5 \text{OK} \), the work of Long et al., has shown that \( \lambda_{12} \ll \lambda_{11}, \sigma_{12} \ll \sigma_{11}, \varepsilon_{11}' \ll \varepsilon_{12}' \), and \( \frac{\sigma_{12}}{\lambda_{11}} \varepsilon_{cn} \) is negligible, hence the quantity \( \varepsilon_{12}'' \) is determined through the measurement of \( \rho_{11}, \gamma_{11}, \) and \( \varepsilon_{12}' \):

\[
\varepsilon_{12}'' = \frac{-\varepsilon_{21}'}{\gamma_{11} \rho_{11}} \frac{\Sigma_{i}^{\text{eff}}}{H} \quad (H \gg H_i)
\]

or

\[
\Sigma_{i}^{\text{eff}} = \left( \frac{3}{\pi^2 k_c^2} \right) \left( \frac{\rho_{11} \gamma_{11}}{H \varepsilon_{21}'} \right) \frac{1}{T}
\]

in terms of the measured coefficients:

- \( \varepsilon_{21}' \), adiabatic Nernst Ettinghausen coefficient
- \( \rho_{11}' \), isothermal electrical magnetoresistance
- \( \gamma_{11}' \), adiabatic thermal magnetoresistance

Determination of the effective density of states \( \Sigma_{i}^{\text{eff}} \) was made from the experimentally measured coefficients. All measurements were made at a field of 12.7 kilogauss which satisfied the conditions under which Eq. (23) was derived \( (H \gg H_i) \). The results of this determination are shown in Fig. 6, where the solid curve represents a least-square fit for a straight line through the experimental points. The intercept of the line at \( T = 0 \) indicates a value of
\[ \Sigma_i Z_i^{\text{eff.}} \left( \text{erg}^{-1} \cdot \text{cm}^{-3} \times 10^{33} \right) \]
\[ \Sigma_{\text{eff}} = (1.0690 \pm 0.0749) \times 10^{33}/\text{erg cm}^3. \]

This value compares favorably with that from other sources based on a computation of the density of states expected from nearly free electron theory:

\[ \Sigma_{\text{elec}} = \frac{3}{2} \sum \frac{n_i}{e_i} \quad (24) \]

most recent results of Windmiller\textsuperscript{65} and Rao\textsuperscript{66} indicate that a value of \[ \Sigma Z_i = 1.07 \times 10^{33}/\text{erg cm}^3 \] should be expected on the basis of nearly free electron theory, a value in excellent agreement with ours.

From the above equation it should be noted that the density of states should be independent of temperature but as others have observed,\textsuperscript{67,68} \[ \Sigma Z_i^{\text{eff}} \] appears to have a \( T^2 \) dependence as shown clearly in Fig. 6. This interesting result has only recently been resolved by the assumption that "phonon drag" occurs to a great extent in measurements on antimony, when at low temperatures, because of the dominance of phonon-electron N-scattering at these temperatures. An explanation of this effect and its bearing on the results of this experiment will be given below.

B. Phonon Drag

The complex theory of the phonon-drag phenomenon in metals becomes most amenable to treatment and experimental verification in substances in which phonon-electron interaction predominates over all other scattering processes efficient in scattering phonons. It was
shown in Section III that this condition was well satisfied in the sample used.

Phonon drag may be understood in either of two equivalent contexts:

1) If one considers a system in which both a thermal and an electrical potential gradient are present, it is usually assumed that under such conditions the phonon distribution is in equilibrium when any interaction with the electron system is being considered. This will not be the case at sufficiently low temperatures when the mean free path of the phonons for interaction with other phonons, impurities, or boundaries is much longer than the mean free path with respect to phonon-electron interaction. For in this case, if an electric current is flowing, momentum will be transferred from the electrons to some of the phonons and this momentum will be unable to be dissipated into the whole phonon system before further electron interaction occurs to increase the momentum still more. Thus the phonons will not be able to come into thermal equilibrium with the rest of the system and can be imagined to be "dragged" by the electrons. The result is an added contribution to the isothermal Peltier coefficient given by

$$\pi_{\text{tot}} = \pi_e + \pi_{\text{drag}} = \pi_e + \frac{C_g T}{3ne} \alpha'$$

(25)

due to the lattice heat capacity $C_g$ carried by the phonons. The coefficient $\alpha'$ is a measure of the relative chance of a phonon to be scattered in a phonon-electron interaction as compared with all
other things a phonon might be scattered by, such as other phonons, impurities, boundaries, etc. Its value ranges from 0 to 1. The factor $1/3$ arises from the assumption that the phonons are an isotropic gas exerting a pressure on the electrons.

Since the heat capacity of the lattice is unusually large compared to the electronic heat capacity in the semimetals due to the small number of conduction electrons, the drag term may produce a profound effect on $\pi$, the isothermal Peltier coefficient.

2) Conversely, if one assumes a fixed temperature gradient (as is the case under most experimental conditions) some momentum will be transferred from the phonons to the electrons resulting in a change in the current flow. Zero current results only when the cold end of the sample acquires enough of an excess of electrons so that their electrostatic field counter balances the combined effect of the "phonon drag" and the normal tendency of the electrons to diffuse from hot to cold. The observed potential gradient is the thermoelectric power

$$e'' = e''_{\text{elec}} + e''_{\text{drag}} = e''_{\text{elec}} + \frac{\xi}{3ne} \alpha' \quad (26)$$

The equivalence of these two approaches is assured by the Onsager relation

$$\hat{\pi} = \hat{\epsilon}_T \quad (27)$$

which must hold in all cases.\textsuperscript{73} The equivalence of results obtained using specific models in both formulations has been confirmed.\textsuperscript{74} The second
of these two formulations applies to the measurements performed in the present study.

Since the drag contribution depends on the lattice component of the heat capacity, \( C_g \), it is ordinarily a negligible effect at very low temperatures in metals. But because the semimetals have several orders of magnitude fewer electrons per unit volume than ordinary metals, the ratio of the heat energy carried by the dragged phonons to the total heat energy transported is much larger in this case, and may produce a marked effect on thermomagnetic transport effects.

The condition of "full" phonon drag is met when the scattering efficiency \( \alpha' \) mentioned above approaches the value 1. It was shown in the Section III that this condition was well satisfied in the present experiment. Thus since \( Z_{\text{elec}} \propto \varepsilon_{\text{elec}}^{\text{"e}} \) as shown in Eq. (21), an effective density of states can be defined by modifying Eq. (26) to read

\[
\sum_i Z_{\text{eff}}^\Sigma = \sum_i [Z_{\text{elec}}^i + Z_{\text{drag}}^i] = \frac{3}{2} \sum_i \frac{n_i}{C_i} + \frac{12}{5} \frac{e^2}{\hbar^2} \frac{N}{\Theta^3} T^2
\]

where the Debye formula has been substituted for \( C_g \) and \( N \) is the number of atoms per unit volume. Substituting the value expected from free electron theory for \( \Sigma Z_{\text{elec}}^i \) from the most recent determinations of \( n_i \) and \( \zeta_i \),

\[
\begin{align*}
n_e &= 5.54 \times 10^{19} \text{ electrons/cm}^3 & \zeta_e &= 19.0 \times 10^{-14} \text{ ergs} \\
n_h &= 5.49 \times 10^{19} \text{ holes/cm}^3 & \zeta_h &= 13.0 \times 10^{-14} \text{ ergs}
\end{align*}
\]
and our own determination of the Debye temperature (see Section V), \( \theta = 209.6^\circ \text{K} \) yields

\[
\Sigma Z_i^{\text{eff}} = (1.07 + 0.610 T^2) \times 10^{33} \text{ erg}^{-1} \text{cm}^{-3}
\]  

(29)

A straight line least squares fit of the experimentally determined quantity \( \Sigma Z_i^{\text{eff}} \) versus \( T^2 \) shown in Fig. 6 gives the coefficients

\[
\Sigma Z_i^{\text{eff}} = (1.069 + 0.5261 T^2) \times 10^{33} \text{ erg}^{-1} \text{cm}^{-3}
\]  

(30)

The agreement between these two equations based on the assumption of "full phonon drag" is quite remarkable. Using for the scattering efficiency, \( \alpha^i = 1 \), and including the factor \( 1/3 \) in Eq. (26), on the assumption that the phonons exert a pressure on the electrons in the direction of the heat flow, appears therefore to have been a reasonable choice of assumptions.

In summary, the magnitude of the effective density of states measured from this experiment has been found to be proportional to the square of the absolute temperature below \( T = 2.4^\circ \text{K} \), a temperature dependence resulting from the effect of full phonon drag. An accurate determination of \( \Sigma Z_i^{\text{elec}} \), free from the influence of the drag effect, was made by extrapolation of \( \Sigma Z_i^{\text{eff}} \) to \( T = 0 \). The value of \( \Sigma Z_i^{\text{elec}} \) thereby obtained agrees with the most recent estimates as shown above.
V. DENSITY OF STATES AND THE ELECTRONIC SPECIFIC HEAT

A. Theory

Measurement of the electronic component of the heat capacity of a metal is both an accurate and a direct method of evaluating the total density of states at the Fermi surface. Free electron theory gives the relation

$$C_{el} = \gamma T = \left(\frac{1}{3}\pi^2 k^2 z_{el}^e E_F\right) T$$

(31)

for the specific heat, where $\gamma$ is the coefficient of the linear term in the electronic specific heat $C_{el}$, $z_{el}^e$ is the number of energy states per unit range of energy at the Fermi energy $E_F$, and where the remaining symbols have the same meaning as previously given.

In most metals, this component of the total heat capacity becomes comparable to the lattice specific heat

$$C_L = \frac{12}{2\pi^2} 4Nk\left(\frac{T}{6}\right)^3 = \beta T^3$$

(32)

at liquid helium temperatures ($N$ is the number of atoms per unit volume). In semimetals however, the electronic term of the heat capacity is a relatively small fraction of the lattice heat capacity even at 1°K, because of the proportionately small number of conduction electrons in these elements, and a further reduction in temperature is required to make an accurate determination of $\gamma$.

In addition to the electronic and lattice components of the specific heat, there appears in the semimetals a term due to the interaction of the nuclear electric quadrupole moment with the electric
field gradient of the crystal. The orientation sensitive term of the nuclear energy when the nucleus is in an axially symmetric field gradient is given by

$$E_m = \frac{e^2 q Q}{4l(2l-1)} [3m^2-1(l+1)]$$

(33)

where $m$ is the projection of the nuclear spin, $l$, on the symmetry axis, $e$ is the electronic charge, $Q$ is the scalar quadrupole moment of the nucleus, and $q$ is the largest component of the electric field gradient tensor in the principal axis system. An energy level system of this form produces a Schottky-type heat capacity anomaly. For temperatures higher than the maximum of the anomaly, the nuclear quadrupole heat capacity $C_Q$ can be expanded in a power series in reciprocal of the absolute temperature, $T^{-1}$. The expression for the first term in the expansion for $C_Q$ is given by

$$C_Q = \frac{R}{80} \frac{(2l+2)(2l+3)}{2l(2l-1)} \frac{(e^2 q Q)^2}{kT} = \frac{\alpha}{T^2}$$

(34)

where $R$ is the universal gas constant.

The total heat capacity of the sample can thus be written as the sum of the contributions due to the nuclear quadrupole interaction, the lattice and the electrons, respectively

$$C = \alpha T^{-2} + \beta T^3 + \gamma T$$

(35)
The most direct manner of determining the values of \( \beta \) and \( \gamma \) from experimentally determined values of the total heat capacity \( C \) for those elements which do not have a nuclear quadrupole contribution is obvious if Eq. (35) is divided by \( T \).

\[
\frac{C}{T} = \frac{\alpha}{T^3} + \beta T^2 + \gamma, \quad \alpha = 0
\]  

(36)

It is seen that because there is no term involving the nuclear quadrupole contribution, Eq. (36) is of the form of a straight line with intercept \( \gamma \) and slope \( \beta \). In the presence of a nuclear quadrupole contribution, it is necessary to include the term \( \alpha T^{-3} \) in Eq. (36). Determination of the values of the coefficients can be accomplished in this case by fitting a polynomial of the form of Eq. (36) to the experimentally measured values of \( C/T \).

B. Results and Discussion

The heat capacity data were analyzed in the following manner. The heat capacity of the sample (and its holder) were measured and the value of the coefficients of the separate contributions \( \alpha, \beta, \) and \( \gamma \) were determined by fitting the data points plotted in \( C/T \) versus \( T^2 \) to Eq. (36). The experimental points are shown in Fig. 7 (upper part) where the solid line represents the result of a least-square fit. In a separate experimental run the heat capacity of the addenda (i.e., the holder, etc., with the sample removed) was determined and the coefficients appropriate to this data were found. The experimental points are shown in Fig. 7 (lower part) where the solid line represents the result of a least-square fit. The coefficients characteristic of the antimony sample alone were then obtained by subtraction.
of the two sets of coefficients. The values obtained are listed in Table I and are compared to the other recently determined values. We find:

$$C = \left[ \frac{0.00197 \pm 0.00023}{T^2} + (0.2110 \pm 0.0053)T^3 + (0.11654 \pm 0.00461)T \right] \text{millijoules/mole deg}$$ (37)

1. Nuclear Quadrupole Heat Capacity

The measured value for the nuclear quadrupole contribution was found to be $(1.97 \pm 0.23) \times 10^{-3}$ millijoules deg/mole. This value differs by a factor of 2 from the result of McCollum and Taylor of $(3.94 \pm 1.49) \times 10^{-3}$ millijoules deg/mole, and falls outside their stated range of error. From theory a value of $4.37 \times 10^{-3}$ millijoules deg/mole is expected if the data from nuclear quadrupole resonance experiments is used to evaluate $\alpha$ from Eq. (34). This is a higher value than was obtained in either specific heat determination, but closer to the results of McCollum and Taylor. It should be noted that this expected value of $\alpha$ varies widely with the value used for the scalar quadrupole moment of the nucleus, $Q$, for which different determinations differ by about 30%. Since in Eq. (34) this parameter is squared, a different value for $Q$ than those obtained from NQR data would tend to shift the value expected for $\alpha$ to as low as $1.9 \times 10^{-3}$ millijoules deg/mole. Because the temperature reached in this work was almost 0.2K lower than that of McCollum, the contribution to the total specific heat
from the nuclear term was appreciably larger than in their work making probably a more accurate determination of the value of $\alpha$ possible.

2. The Lattice Heat Capacity

The slope of the linear portion of the plot of $C/T$ versus $T^2$ (Fig. 8) is a measure of the Debye temperature $\Theta$, as seen from Eq. (36) through the relation

$$\beta = \frac{12}{5\pi^4} N k \left(\frac{1}{\Theta}\right)^3$$  \hspace{1cm} (38)

We find $\beta = 0.2110 \pm 0.0053$ millijoules mole$^{-1}$K$^{-4}$ and $\Theta = 209.60^\circ$K.

Measurements of $\beta$ down to temperatures of 0.7$^\circ$K and 0.5$^\circ$K have been made by Culbert$^{87}$ and by McCollum and Taylor$^{88}$, respectively. The present work was carried down to 0.37$^\circ$K. Their values are shown in Table I together with the value determined in the present work; agreement with both authors is good. It has been argued (see next subsection, table of $C_q$ values) that the large contribution, $C_q$, in the semimetals influences the slope of the specific heat curve (Fig. 8) below 1$^\circ$K to such an extent that a more accurate determination of $\beta$ (and thus $\Theta$) is thwarted. The temperature dependence of $\Theta$ at low temperature is a well known phenomenon$^{89}$ and may itself account for the discrepancies between the results in Table I, since the measurements made by the authors listed in Table I covered different (but overlapping) temperature ranges.
\[ C = \left( \frac{0.00197 \pm 0.00023}{T^2} \right) + \left( 0.2110 \pm 0.00530 \right) T^3 + \left( 0.11654 \pm 0.00641 \right) T \] 
\[ \times 10^{-3} \text{ J/mole} \cdot \text{K} \]

\[ \frac{1}{3\pi^2} k^2 \sum Z_i^{\text{eff.}} = \left( 0.1232 \pm 0.00978 \right) + \left( 0.060643 \pm 0.00118 \right) T^2 \] 
\[ \times 10^{-3} \text{ J/mole} \cdot \text{K} \]
### TABLE 1. Comparison of Specific Heat Data.

\[
\frac{C}{T} = \frac{\alpha}{T^3} + \beta T^2 + \gamma
\]

<table>
<thead>
<tr>
<th></th>
<th>Present Work</th>
<th>McCollum and Taylor</th>
<th>Culbert</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Range (°K)</td>
<td>0.37 - 1.40</td>
<td>0.5 - 1.1</td>
<td>0.7 - 4.0</td>
</tr>
<tr>
<td>(\alpha (\frac{\text{mJ}}{\text{mole deg}}))</td>
<td>0.00197±.00023</td>
<td>.00394±.00149</td>
<td></td>
</tr>
<tr>
<td>(\beta (\frac{\text{mJ}}{\text{mole deg}}))</td>
<td>0.2110 ±.0053</td>
<td>0.2011 ±.0034</td>
<td>0.2099</td>
</tr>
<tr>
<td>(\Theta (°K))</td>
<td>209.60</td>
<td>213.01</td>
<td>210.2±1.0</td>
</tr>
<tr>
<td>(\gamma (\frac{\text{mJ}}{\text{mole deg}}))</td>
<td>1.11654±.00641</td>
<td>1.11010±.00039</td>
<td>1.03 ±.004</td>
</tr>
<tr>
<td>(Z_{\text{el}} 10^{33})</td>
<td>1.0110±.0460</td>
<td>0.95516±.00338</td>
<td>0.8936±.0034</td>
</tr>
</tbody>
</table>
3. The Electronic Specific Heat

Accurate measurement of the electronic component of the total heat capacity of antimony (and of the other semimetals) is especially difficult because of its small number of conduction electrons. The lattice heat capacity term dominates over the electronic term down to very low temperatures and accounts for $75\%$ of the total even as low as $1^\circ K$. The relative contribution of the three components is shown in the table below at temperatures of $1^\circ K$ and $0.5^\circ K$.

<table>
<thead>
<tr>
<th>T</th>
<th>$C_Q$</th>
<th>$C_L$</th>
<th>$C_{el}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0^\circ K$</td>
<td>10$%$</td>
<td>75$%$</td>
<td>24$%$</td>
</tr>
<tr>
<td>$0.5^\circ K$</td>
<td>21$%$</td>
<td>35$%$</td>
<td>44$%$</td>
</tr>
</tbody>
</table>

It can be seen from the table that difficulty is also encountered if measurements are taken at too low a temperature because of the increasing importance of the nuclear quadrupole contribution. One must thus utilize the range of temperature between $0.5^\circ K$ and $1^\circ K$ for the measurement of the electronic contribution, depending on computational methods to take account of that portion of the total heat capacity measurement which is contributed by the electrons alone.

In view of these difficulties, considerable variance would be expected in the results obtained by different workers, but unusually good agreement has been found in three recent measurements (see Table I).

The value of $\gamma$ found in the present experiment was $(0.11654 \pm 0.00041)$ millijoule mole deg$^{-2}$, shown as the intercept of the extrapolation of
the upper curve to the C/T axis in Fig. 8. This value corresponds to an electronic density of states $Z_{E_F}$ [through Eq. (31)] of $1.011(10^{33}$ erg cm$^{-3}$). McCollum and Taylor and Culbert find for $\gamma$, values of $(0.1101 \pm 0.00039$ millijoules/mole deg$^2$) and $(0.103 \pm 0.004$ millijoules/mole deg$^2$), respectively. It may be noted that all three experimental values are outside the limits of error claimed by the other two authors.

One possible explanation of the discrepancies may be due to the purity of the samples used in each case. It is known that in antimony the valence band is almost exactly filled and, under these conditions, the density of states at the Fermi surface would be extremely sensitive to the presence of impurities. The antimony used in this experiment was 99.9999% pure but information is lacking as to the purity of the samples used by the other authors. The agreement however, in the values of $\gamma$ is still remarkable considering the difficulties in measurement cited above.

In view of the foregoing considerations and results, an independent measurement of $\gamma$ by a method not susceptible to the pitfalls involved in specific heat measurement in antimony would be of obvious value. Such a measurement was the object of the research reported in Section IV; it will be compared with the present results below.

4. Comparative Analysis

Measurement of the density of electronic states of antimony through transport experiments yields a value $Z_{E_F} = (1.0690 \pm .0749) \times 10^{33}$ erg$^{-1}$ cm$^{-3}$, which when compared to the value we obtained for $Z_{E_F}$ (specific heat), gives $Z_{E_F}^{\text{Sp.H}} = 1.0110 \pm .0460 \times 10^{33}$ erg$^{-1}$ cm$^{-3}$. 
There is clear agreement between the values for the density of states as determined through these two independent methods, within experimental errors. This is shown in Fig. 8, where $C/T$ and $\Sigma Z_i$ have been plotted in the same units. The respective intersects are proportional to the density of states. The fundamental interest of Fig. 8 is that it allows a comparison between the total specific heat of the lattice $C_L$ and that part of $C_L$ which is transported by the electrons through "phonon drag". One finds $C_{\text{drag}}/C_L = 0.32$. This $1/3$ factor is expected on pure kinetic grounds, where the phonons are assumed to behave like an isotropic gas and to exert a pressure $p$ on the conduction electrons given by $p = \frac{1}{3} U(T)$ where $U(T)$ is the energy density of the phonon gas. The existence of the $1/3$ ratio above means then that in Eq. (25), $\alpha' = 1$: One has a "full" phonon drag, the electrons interacting with the entire phonon system, i.e., with both longitudinal and transverse polarizations. This results from the fact that in such an anisotropic medium, there are no purely transverse waves, i.e., even with transverse waves there is associated a certain amount of density variation of the lattice and by consequence a certain amount of interaction with the electrons.

We finally investigate the question of uncoupling of the interaction between the longitudinal and transverse lattice waves at temperatures below 1.5°K. It is seen from the experimental results that this has no effect on the phonon drag. We also proposed that it was responsible for the added contribution to thermal conductivity. This is understood along the following lines: As long as the two polarization systems are highly coupled, their phonon mean free path
are per force equal: $\Lambda_T^p = \Lambda_L^p$. As the temperature is lowered, and the coupling becomes loose, both systems still interact with the electrons (phonon drag unchanged) but the mean free path of the transverse waves $\Lambda_T^p$ becomes larger than $\Lambda_L^p$, in accord with the smaller amount of density variation it creates. One has now $\Lambda_T^p > \Lambda_L^p$, and a larger thermal conductivity obtains. As $\Lambda_T^p$ increases, additional scattering mechanisms (e.g. isotope scattering) intervene to limit its growth.
VI. CONCLUSION

The attack on the problem of the electronic density of states of antimony through its determination by 2 independent experimental methods has been very successful. The excellent agreement obtained from thermoelectric phenomena at high magnetic fields and from specific heat measurements shows that earlier discrepancies found in the literature were due to the limitations of the temperature range. Extrapolations of the thermoelectric results to 00K are reliable only if measurements are carried below 10K. This gives added confidence in the conclusions drawn from transport effect studies.

The other achievement of this study is the clear-cut $T^2$ dependence demonstrated for the low temperature thermal conductivity of antimony, thus confirming predominance of phonon-electron scattering in a pure element, when it had been heretofore observed only through alloying.

Similar transport effect studies in bismuth and arsenic, in the He$^3$ temperature range, would probably be revealing.
APPENDIX

Part A: Transport Measurements

Crystal

The crystal was prepared initially and used by Dr. Jerome Long in his experiments involving transport phenomena in antimony at temperatures between 1.6°K and 4.0°K. It was decided that in using this same crystal, the results obtained in this experiment could extend portions of his data to a temperature of 0.4°K.

The crystal was cut with a Servomet spark cutter from a zone-refined bar obtained from Cominco, the stated purity of which is 99.99999% /1. Flat surfaces perpendicular to the trigonal axis were obtained by cleavage. The crystal was then cut into the shape of a right parallelepiped with the width of the crystal along a binary axis. The dimensions were 20 X 4.6 X 2 mm.

A period of 12 months elapsed between the present measurements and those of Dr. Long. Though the crystal was carefully handled and stored during the interim, certain ageing and diffusion processes may have lowered somewhat the purity of the crystal.90 Traces of self-cleavage were present at one end of the crystal.

Before mounting, the crystal was carefully cleaned with an acid solution.91 Traces of Bi-Cd solder were cleaned from the surface where the probes had previously been soldered. Care was taken to solder the new probes between the locations of the previous probes.
The transverse and longitudinal probes were soldered to the crystal with the aid of a microscope; solder "dots" did not exceed a diameter of .063 cm. Attachment of all probes was completed before the crystal was soldered to the sample holder so as to prevent straining the crystal.

**Helium-3 Refrigerator**

(1) Basic Construction

(a) Pumping and Storage System

The means of reaching and maintaining temperatures below 10K was by use of a helium-3 refrigerator, shown schematically in Fig. 9. The system was similar to one constructed by Garwin and Reich,\(^\text{92}\) with the helium-3 gas stored between runs in the casing of a shaft-sealed Welch 1402 KGB vacuum pump by means of an arrangement of valves. A mercury manometer sealed to the interior storage space provided a check on the continuing vacuum tightness of the storage space between runs as well as a method of measuring the gas pressure on the exhaust side of the pump during a run. An automatic electrical switch-off device whose sensing element was mounted on the manometer could be activated to prevent an explosive buildup of pressure should any part of the helium-3 system begin leaking during a run.

(b) Trapping and Vapor Removal System

Removal of oil vapor and air contaminants from the recirculating He\(^3\) gas was accomplished by placing first a glass tube stuffed with copper wool and then a brass cannister
filled with activated cocoanut charcoal in the exhaust line of the pump. These traps remained submerged in liquid nitrogen during the runs assuring removal of any contaminant which might later freeze out at helium-4 temperatures, clogging the return line. The vapor trap housing the copper wool was made of non-permeable "lead" glass to assure visual monitoring of the amount of trapped oil. Further trapping was accomplished by a copper wool trap in the helium-4 bath. This trap, denoted as CD, Fig.10, served as the condenser for the returning helium-3 gas.

(c) Low Temperature Section

The helium-3 gas after condensation passed through a small (1/16 " o.d.) stainless steel tube to the interior of the He^3 pumping line, P, and then through a copper capillary (.011 inches i.d.) spiral which throttled the flow of the liquid-gas mixture. The liquid dropped from the end of the capillary into a cavity E, formed by one extremity of the copper sample holder. A spiral of 0.005 inch thick, 1/2 inch wide copper strip soldered inside this cavity prevented vertical temperature gradients from developing as the resultant pool of liquid helium-3 was pumped. This fin assembly was serrated on its lower edge to permit freedom of flow of the helium-3 liquid and then soft soldered to the base of the cavity. The copper sample holder was thus cooled and subsequently held at the temperature of this He^3 liquid bath.
The vapor from the bath was pumped through a 1/2 inch o.d. by .010 " wall stainless steel tube P, four inches long, exerting precooling influence on the incoming He³ liquid in the copper capillary, CA, Fig. 10. This pumping line terminated at its upper end at the base of a one inch i.d. brass flange and collar, F, housing a three stage radiation trap (see Fig. 10) kept cool by the outer He⁴ bath. Two subsequent radiation traps at higher levels in the one inch o.d. by .010 " wall pumping line, L, prevented radiation from entering the low temperature section. Outside of the dewar system the pumping line widened to 2 inch diameter. The pumping speed of the forepump was bolstered at the end of this line by a liquid nitrogen cold trapped 3 inch diameter booster diffusion pump. Mechanical vibration transmitted to the dewar system by the forepump was held to a minimum by inserting a 4 foot long stainless steel bellows section which was damped by fastening it to a heavy steel cylinder.

(2) Operation

(a) Preparation and Precooling

Of absolute importance in the operation of any helium-3 refrigerator system is the assurance of an absolutely vacuum tight system, especially with respect to helium-4 leakage which may occur in the low temperature section of the equipment in the form of superfluid leaks. Even a small amount of helium-4 in the helium-3 liquid produces
a lowering of the vapor pressure which is not immediately apparent, and which might easily cause gross errors when calibrating a secondary thermometer against this pressure. For this reason, this system was designed to be permanently sealed in the low temperature portion; the evaporator was incorporated on the interior of the sample holder making it unnecessary to break the seal of the He\textsuperscript{3} system if it were necessary to change the sample. Furthermore, a mass spectrometer leak detector\textsuperscript{93} was used to test for leaks both at room temperature and at liquid nitrogen temperature before releasing the helium-3 gas into the helium-3 system.

Evacuation of the helium-3 system was provided by an oil diffusion pump and forepump connected to the 2 inch helium-3 pumping line by a 2 inch Vecco bellows sealed valve. This arrangement facilitated rapid and complete evacuation of the helium-3 system which was to be important in the subsequent operation of this refrigerator as will be explained below.

The helium-3 refrigerator was prepared for operation by evacuating it at room temperature to a pressure of approximately $3 \times 10^{-6}$ mm Hg. by opening valve D (see Fig. 9). Leak testing was performed by putting one atmosphere of pure He\textsuperscript{4} gas into the helium-4 dewar bath space BA (Fig. 10) while the leak detector was attached to the helium-3 system. If no leak registered, helium-4 gas was sprayed liberally
around all external joints of the helium-3 system. If the whole system proved leak tight, then preparations for pre-cooling were begun.

The ultimate success in the operation of a helium-3 refrigerator depends on the degree of thermal isolation of the evaporator E and sample holder S at temperatures below 4.2°K. However, some degree of thermal linkage to the exterior environment must be available during the precooling stages. Several methods to achieve both of these ends were tried, and a suitable combination finally was adopted.

The "insulation vacuum" space, IV, surrounding the sample holder was flushed several times with helium-free nitrogen gas. Care was exercised to use only virgin gum rubber tubing and a forepump which had never been used for pumping helium gas in the evacuation and admission of the helium-free nitrogen gas into the insulation vacuum space. This hose was cut into three sections, then the pieces connected together by a "tee". One free end was attached to the forepump, one to the insulation vacuum pumping line, IVL, and the third end was immersed in a flask of liquid nitrogen. Hose-clamps on the liquid nitrogen and forepump branched could be manipulated in turn to first evacuate the system, fill it with nitrogen gas (evaporated liquid nitrogen), then re-evacuate it. This process was repeated three or four times. Liquid nitrogen was used as the supply of
nitrogen gas because it was felt that this was the most helium-free nitrogen available. After the last flushing, the insulation vacuum was pumped to a pressure of approximately 100 microns and sealed off by closing valve 1 (Fig. 10).

Subsequently, when liquid nitrogen was added to the outer flask of the experimental apparatus, heat was extracted from the sample holder through the weak atmosphere of nitrogen gas remaining in the insulation vacuum, and through exchange gas in the helium-4 dewar, BA. This pre-cooling was maintained for eight to twelve hours before transferring liquid helium-4 into its flask.

When helium-4 liquid was transferred, the nitrogen remaining in the insulation vacuum froze out on the inner walls of the can B, leaving a very high vacuum. To bring the temperature of the sample holder the remaining way from liquid nitrogen temperatures to liquid helium temperatures, approximately 100 mm Hg pressure of helium-4 gas was admitted to the helium-3 system through valve E (Fig. 9). After the outer bath had been pumped below 100 mm Hg. pressure, the gas in the helium-3 system condensed on the interior of brass flange BF, (Fig.10) dripped down pumping tube P, evaporated at E, and recondensed at BF, providing a cooling effect by this refluxing action of the helium-4. This cooling was enhanced
by pumping the outer bath below the \( \lambda \) point, allowing
the Rollin film to add to the cooling of the sample holder.
Depending on the degree to which the sample holder had
been precooled, a time of one to two hours was required
before the sample holder reached the temperature of the
outer bath.

At this point valve D (Fig. 9) was opened and the helium-3
system was pumped to a pressure of \( 1 \times 10^{-5} \) mm Hg, leaving
only one part helium-4 to \( 10^7 \) parts helium-3 gas, when it
was added later, a level of contamination much lower than
that of new "uncontaminated" \( \text{He}_3 \) gas.94

(b) Continuous Operation

After setting the vapor pressure sensing tube gauge to a
reading of zero pressure, valve D was shut, liquid
nitrogen was added to the foreline vapor traps, and the
helium-3 forepump was started. With the pump "by-pass"
valve C shut, (Fig. 9) valves A and B could be opened,
releasing the helium-3 gas into the helium-3 system and
beginning the "continuous" mode of operation. Cooling of
the sample holder from any temperature between 4.2 and
1.2°K to a temperature of approximately 0.7°K required only
two or three minutes. The lowest temperature attainable
in continuous operation was strongly dependent on the
temperature of the helium-3 liquid dropping into the
evaporator, that is, strongly dependent on the temperature
of the outside bath where the helium-3 gas was condensed at the condenser CD.

(c) Batch Operation

The "batch" mode of operation was begun, when lower temperatures were desired, by closing valve A, thus recollecting the evaporating liquid helium-3 in the pump. The optimum conditions for beginning batch operations could be determined by monitoring the manometer on the helium-3 pump. When the manometer showed a minimum value, as much helium-3 was condensed in the low-temperature section as was possible; thus when valve B was shut, the "batch" of liquid helium-3 would last a maximum length of time. With no heat input to the sample holder, a single "batch" would last for several hours. Even with appreciable heat input, the liquid would remain more than two hours before recycling was required. The minimum temperature attainable in batch operation was about 0.36°K with both diffusion pump and forepump operating, and about 0.39°K with the forepump alone.

(3) Temperature Regulation

(a) Manual

Regulation of the He³ bath temperature could be maintained manually while in the continuous mode of operation by partially opening the "by-pass" valve C on the helium-3 forepump (Fig. 9). This valve was a specially made high quality throttling valve which made possible finely
adjustable back flow rates and thus when in use, allowed fine control of the pumping speed of the forepump. Any desired temperature between 0.65°K and 1.0°K could be attained through the use of valve C, but it was found that, if left at a given setting, a slow drift in the temperature of the helium-3 bath occurred. However, a skillful operator could adjust valve C so as to keep the bath temperature constant to within one millidegree over a period of twenty minutes.

(b) Electrical

In batch operation, since valve A was closed, valve C could not be used for temperature regulation; thus an electrical heater feed-back system was developed to control the temperature in the region below 0.65°K. The regulation circuit consisted of a 10 Ω, 0.1 watt Allen Bradley resistor used as a temperature sensing element in one arm of a Wheatstone Bridge circuit, a photocell placed to receive an increasing portion of the beam of a D'Arsonval galvanometer serving as the null detector of the bridge, an A-C amplifier to enhance the signal of the photocell and, when rectified, to supply the signal to a non-inductive heater wound directly on the sample holder. The regulator was put into action by setting the adjustable arm of the bridge circuit to a resistance corresponding to the resistance of the AB sensing thermometer (resistor) at the desired temperature. As the sample holder was cooled by
the He\textsuperscript{3} refrigerator to a temperature for which the bridge neared balance, the beam from the galvanometer fell on the photocell activating the regulating heater until the resistance of the sensing thermometer restored the galvanometer to a slightly off-balance position. Oscillations in the feedback circuit could be controlled by adjusting the damping resistance of the galvanometer and controlling the sensitivity of the galvanometer through an Aryton shunt box.

This method of temperature regulation could achieve a stability of one millidegree over a thirty minute period, which was sufficient time to make the necessary measurement at that given temperature. It was found, however, that since heat had to be supplied at a rate high enough to offset the cooling effect of the He\textsuperscript{3} pump at its maximum pumping speed, oscillations were easily induced by small disturbances in the temperature of the sample holder, such as the heating produced by eddy currents in the sample holder when the magnetic field was changed.

It was found in continuous operation that the performance of this regulator could be materially improved by adjusting the He\textsuperscript{3} pump to a value slightly higher than that needed for the desired temperature. Thus the heat input necessary to regulate the temperature was materially reduced, and the dynamic balance of pumping against heating was inherently more stable. This option, while possible in
continuous operation, was not available in batch operation.

(4) Vapor Pressure Thermometry

(a) General

Since the temperature of He\textsuperscript{3} liquid is a well determined function of its vapor pressure,\textsuperscript{97} and since very pure (vapor pressure standard) helium-3 gas was used in this experiment, the secondary thermometers could be calibrated directly against the vapor pressure of the helium-3 bath.

The vapor pressure of the liquid could be measured under either dynamic or static conditions by means of a 3/16 inch o.d. by .010 inch wall stainless steel tube, SL, passing through the liquid helium-4 into the helium-3 system, terminating at the upper end of pumping tube P (see Fig. 10). If a secondary thermometer is to be used during the experimental run, it has been found quite satisfactory to calibrate it against the vapor pressure of the helium-3 by stopping the pumping on the helium-3 bath at its lowest temperature, and letting it warm up slowly, monitoring the pressure at intervals over the two or three hour warm-up period.

(b) Pressure Sensing Instrument

The instrument used in this experiment to measure the pressure in the sensing tube was a quartz bourdon tube type instrument made by Texas Instruments.\textsuperscript{98} The tube used was intended to be used in measuring pressures below 200 mm Hg. The sensitivity was such that a pressure 100 microns could
be read with 10\% accuracy and a pressure of 1 mm with 0.1\% accuracy. The instrument gave readings which were strictly reproducible and was found to retain its zero setting over long periods of time. Its sensitivity (1 scale division = 2.5813 microns Hg.) and range made it an ideal indicator for the vapor pressure of the helium-3 bath, especially at lower pressures than could be measured accurately with an oil or mercury manometer and with more speed than with a McLeod gauge.

(c) Pressure Sensing Methods

Design of the pressure sensing tube is important in He\(^3\) vapor pressure thermometry because large corrections to the pressure which is indicated at the warm end of the sensing tube become necessary if the vapor pressure nears the free molecular flow state.\(^9^9\) Attempts have been made to graduate the sensing tube at levels of sharp temperature change so as to cancel this thermomolecular effect,\(^1^0^0\) but the simplest method was found to be that of employing a single tube of uniform diameter since the correction factors are known to a high degree of precision.

(5) Critique - Design Considerations of He\(^3\) Refrigerators

(a) Continuous Operation

The temperature of the helium-3 bath when in continuous operation was found to be strongly dependent on the lowest temperature attainable in the helium-4 bath. The dependence was caused almost entirely through the fact that the liquid


He\textsuperscript{3} entering the low temperature bath through capillary CA was at the temperature of the outside bath. It was found that a 0.1 degree rise in the temperature of the outside bath at 1.2°K produced a nearly equivalent rise of temperature in the He\textsuperscript{3} bath. In batch operation, this effect was eliminated, because there was no re-admission of He\textsuperscript{3} to the low temperature section, and the lowest temperature of the system dropped from approximately 0.65°K to approximately 0.38°K. For an outside bath temperature below 2°K, radiation to the sample holder from the walls of the can was found to be quite negligible.\textsuperscript{101}

The temperature stability of the helium-3 bath while in the continuous mode of operation was also found to be a strong function of the temperature stability of the outside bath. Stability was much improved when a temperature regulator\textsuperscript{102} was activated on the helium-4 bath.

(b) Batch Operation

In batch operation temperature stability was not affected by fluctuations in the helium-4 bath temperature, but certain other effects became increasingly damaging to stability as lower temperatures were reached. Eddy currents produced in the copper sample holder when the magnetic field was changed were a quite serious source of heating. Vibrations also proved to have an appreciable effect in later parts of the experiment when the sample was not thermally shorted to the refrigerator. Certain of the
vibrational heating problems were relieved by turning off all pumps while measurements were being taken, but it was felt that some vibrational heating remained. Even a gentle tapping of a pumping line was sufficient to cause a very noticeable heating in a thermally isolated sample at very low temperatures.

(c) Running Time

Radiation into the helium-3 system began to cause an unstable warming trend when the liquid in the outer bath left the lowermost radiation trap and brass flange out of the liquid He\textsuperscript{4}. By retransferring, this problem could be quickly remedied in a manner described in the next paragraph.

A remarkable feature of helium-3 refrigerators is the small amount of liquid helium-3 necessary to produce low temperatures for long periods of time while in batch operation. If a sufficient helium-4 supply can be maintained, a single batch (about 0.6 cm\textsuperscript{3} of He\textsuperscript{3}) can last many hours, for low heat inputs. A real limitation to the maintenance of temperatures below 0.5\textdegree K over long periods of time, then, is the lifetime of the helium-4 bath under pumping. In this experiment, this lifetime was approximately four hours. However, it was found to be quite feasible while in batch operation, to warm up the outer bath to 4.2\textdegree K, transfer, and pump down to 1.2\textdegree K again with only a 20\% loss in the He\textsuperscript{3} bath liquid. Using this method, the sample holder was kept at a temperature below 0.5\textdegree K for 16 hours without difficulty.
(d) Vapor Pressure Measurement

A factor found to seriously disrupt the use of the vapor pressure above the helium-3 bath for thermometry purposes was the presence of epoxy resin in contact with the sample holder and evaporator. The thermal conductivity of this resin became extremely low at helium-3 temperatures, and, coupled with a characteristic high heat capacity common to plastics, the effect was to provide a steady heating source to the evaporator section of the helium-3 refrigerator for quite a long time. It was possible to use the indicated vapor pressure of the liquid He\(^3\) as a calibration for the secondary carbon resistance thermometers only after it had been determined that the epoxy had been completely cooled down, which required in excess of ten hours. It is recommended that such materials be excluded from the low temperature portions of He\(^3\) refrigerators whenever possible to avoid this complication.

Sample Holder-Evaporator

The sample holder and helium-3 evaporator were built as an integral unit to reduce occurrence of thermal boundary resistance between the sample and the He\(^3\) bath. A stainless steel tube D, (Fig. 1) 1/2 inch o.d. by .010 inch wall by four inches long served as the pumping tube, the support for the sample holder, and as a thermal insulator from the 1.2\(^0\)K brass flange to which it was connected at its upper end. This tube was sealed to the sample holder
by epoxy resin R, which electrically isolated the sample holder from the main part of the equipment. The heater, RH, for the temperature regulating circuit was wound non-inductively around the exterior of the evaporator portion of the sample holder just below a shoulder provided for securing a radiation shield, which proved to be unnecessary. The sensing thermometer, STh, used in the temperature regulating circuit, was placed near the sample, Sb, as indicated. (Fig. 1)

Part B: Specific Heat Measurements

Crystal

The sample used for measuring the specific heat of antimony was a bar of 142.429 grams mass cut from the same parent bar of antimony from which the crystal for the first part of this experiment was obtained. The sample was approximately 5.0 cm in length and 5.07 cm$^2$ cross section. It was cut to shape and cleaned in the same manner as previously indicated. A large single crystal occupied most of the volume of the specimen.

Only minor adaptation of the helium-3 refrigerator used in the previous part of the experiment was necessary to perform the specific heat measurements.

Sample Holder-Evaporator

(1) Construction

By necessity in this particular type of measurement, a heat switch was necessary in the low temperature section in order to alternately cool and then isolate the sample from the He$^3$ refrigerator. Thus a new evaporator-sample holder was constructed for
this part of the experiment, as shown in Fig. 2. Its design was based on the use of artificial pitch-bonded graphite as a parallel heat shunt to a conventional lead wire superconducting heat switch.

Employing graphite in this manner has four distinct advantages. They are as follows:

1. The thermal conductivity of this form of graphite is higher than many metals at room temperature, relieving some of the problems of precooling the sample.

2. The thermal conductivity of graphite below 10 K is as low as nylon and is much lower than such other commonly used materials as Pyrex, Perspex and teflon.

3. Its rigidity and strength at low temperatures makes it ideal as a rigid support for the sample, eliminating low frequency vibrational heating at low temperatures often encountered with nylon thread-type suspension.

4. Its ability to strongly absorb gas at low temperatures aids in maintaining a good vacuum within the calorimeter, and assures that "gas migration" that may take place involves condensation on the supports near the evaporator, rather than on the sample.

In Fig. 2 the physical arrangement of the three graphite rods APBG used as supports between the sample holder plate PL and the evaporator E is illustrated. The lead wire Pb, used as the heat switch, was approximately .001 inch in diameter and is shown
supported at its upper and lower extremities by pieces of copper shaped to receive and support it. This extremely fine wire was drawn by the Wollaston process and attached to the copper support fingers by bismuth-cadmium solder. The three graphite support rods themselves were about eight centimeters in length and three millimeters in diameter. Their ends were copperplated and soldered into three equally spaced sets of holes in the evaporator and sample support plate with bismuth-cadmium solder. Both the evaporator and sample support plate were made of copper.

The design of the evaporator cavity differed slightly from the one used in the previous part of the experiment. First, the base of the cavity was made wide and flat to achieve maximum exposure of the liquid He$^3$ surface to evaporation. Second, the spiral copper fin assembly used in this cavity was soldered at its outer edge to the side of the cavity so as to leave the base of the cavity free from solder, thus achieving both the advantages of uniform vertical temperatures within the He$^3$ bath, and good heat transfer between the liquid and the evaporator both through the spiral fin and the clean copper floor of the cavity.

The sample Sb itself was attached to the base of the sample holder plate with a minimum of bismuth-cadmium solder. The sample heater was the same one as described earlier and was soldered near the top of the crystal. The standard technique of using tinned constantan wire as current leads to the heater was used for this measurement. The carbon resistor thermometer was
one of the pair used in the first part of the experiment. It was calibrated by attaching it directly to the evaporator in a preliminary run, and reading its resistance as a function of the vapor pressure of the He\textsuperscript{3} bath as described previously. Then for the specific heat measurements, the thermometer was resoldered to the sample at a point near the sample holder plate as indicated in Fig. 2.

(2) Precooling Considerations

Cooling the sample to liquid helium temperatures presented much more of a problem in this part of the experiment because the sample was not in direct thermal contact with the evaporator. The conductivity of the graphite support rods in the range below 77\textdegree K was much lower than at room temperature. A great deal of difficulty was encountered after precooling in the usual manner in finding a method to cool the sample the remaining way without losing the thermal isolation needed once helium temperatures were reached.

One method which was tried involved using a few microns pressure of very pure hydrogen gas as an exchange gas in the space surrounding the crystal, assuming that the hydrogen would "freeze out" and have negligible vapor pressure at sufficiently low temperatures. On trying this approach, it was found that the hydrogen gas before freezing out produced no appreciable cooling to the sample as liquid helium\textsuperscript{4} was transferred into its bath space, even if the transfer was performed extremely slowly.
Another method was developed which bypassed the need for exchange gas and, though time consuming, was found to be best experimentally, as the vacuum surrounding the sample did not have to be violated. This method was an extension of the method described for cooling the evaporator and sample holder for the transport measurements. Helium-4 gas was introduced into the helium-3 system, after transferring liquid helium into the He⁴ flask, but the bath was left unpumped, and a pressure of He⁴ gas slightly in excess of one atmosphere was maintained in the He³ system. This provided for the "refluxing" mode of cooling as was described earlier.

The outer bath was unpumped to conserve helium because the cooling down process to 4.2 degrees required about eighteen hours. So complete was the thermal isolation of the sample that if no He⁴ gas were admitted to the helium-3 system after transfer into the outer flask, the temperature of the sample (in one instance) remained at its precooled temperature of 77°K for eight hours. When the sample reached a temperature of 4.2°K, its heat capacity was low enough to allow cooling to He³ temperatures in a matter of minutes when the helium-3 refrigerator was started.

(3) Operation of the Heat Switch

The superconducting heat switch was "closed" by increasing the magnetic field supplied by a Weiss magnet surrounding the experimental dewar to a field slightly over 800 gauss. This provided good thermal linkage between the sample and the evaporator.
The sample could be cooled in this manner to a temperature of approximately \( -37^\circ\text{K} \) indicating little or no thermal gradient between the sample and cooling source.

When it was desired to "open" the heat switch in order to thermally isolate the sample and begin measurements, the magnetic field was reduced slowly by a field sweeping drive so as to reduce the rather pronounced heating due to eddy currents.

**Measurement Technique**

The technique of measuring the heat capacity of the sample, once isolated, was the standard "temperature drift" method\(^{108}\) illustrated in Fig. 11. Heat is supplied to the sample at a known rate, for a known period of time in this method, and the "before" and "after" temperature drift rates of the sample were extrapolated to the center of the heating period; the values of the thermometer indicated at the intercept of these traces and the line indicating the center of the heating period were averaged to determine the "mean temperature" of the sample during the heating period, and the difference of these values was the temperature increment associated with the energy input to the sample. From this information the heat capacity of the sample is simply,

\[
C_p = \frac{(\text{heater power} \times \text{length of heating period})}{(\text{temperature difference})}
\]

A schematic diagram of the measuring circuitry is shown in Fig. 12. The temperature of the sample was measured as a function of time by
Fig. 11
Typical Temp. Variation

Sample Temp.

$T_f$

$T_i$

Time

$t_1 \rightarrow t_2$

$dT = T_f - T_i$

$\bar{T} = \frac{T_f + T_i}{2}$

Typical Recorder Trace

Heater On

Heater Off

Change Pot. Bias

Bias = 10,000μV

Balance Line

$B = 7000\mu V$

Fig. 12
bringing the voltage drop across the carbon resistor thermometer attached to the sample into approximate balance on a Rubicon potentiometer, amplifying the off-balance reading by a d-c amplifier and recording the output with a Brown stripchart recorder. The recorder was modified so that its pen position at the potentiometer balance was at the center-line of the paper. The bias voltage on the potentiometer was set so that the recorder pen was drifting toward the balance position. When the trace nearly reached the mid-line, a given amount of heat was supplied to the heater on the sample; at the same time the potentiometer was quickly rebiased to a lower setting by such an amount that the recorder trace again approached balance. At this point the heating was ended and the drift rate returned to its former low value. Thus when the "before" and "after" drift rates were extrapolated to the center of the heating period, those extrapolated points on the stripchart recorder were not far from balance and aside from small corrections for the off balance position, the resistance values were given with good accuracy by the bias setting of the potentiometer divided by the thermometer current. In order to prevent any self heating effect in the thermometer, its current never exceeded 0.2 microamperes.

The resistance of the heater was almost totally independent of temperature in the range in which measurements were taken. Thus a measurement of the current and voltage drop across the heater several times during the run by means of a K-3 Leeds and Northrup potentiometer was quite adequate to determine the heat input to the
sample to within .015°/o accuracy. The heater circuit was activated by closing a mercury switch, so employed to eliminate power input uncertainty caused by the electrical noise made in closing and opening a mechanical-contact type switch. An electronic timer was connected to the switch and was activated automatically when the switch was closed. Its readings were accurate to $10^{-6}$ seconds. A double-pole quadruple-throw switch in series with the three volt battery supply for the heater allowed a selection of 0.2 to 6.0 microwatts heater input values. It was found in practice that heater inputs of 1.0 to 6.0 microwatts were most appropriate with heating periods of two to six seconds. The temperature rise of the sample was not allowed to exceed 10°/o of the mean temperature of the crystal at measurement, and in practice ranged between 3°/o and 7°/o of $T_{\text{mean}}$. Measurements could be taken either in a warming or cooling drift rate trend, depending on whether the sample temperature was below or above that of the evaporator. The best results were obtained by cooling to the lowest temperature possible with the heat switch closed, opening the heat switch, stopping the He$^3$ pump and allowing the evaporator to warm up slowly with the crystal as measurements were taken.

The heat capacity of the addendum was taken measured by making measurements with 85°/o of the sample taken away, being careful to remove nothing but pure antimony, leaving all solder, the heater, the thermometer plus the part of the original sample which was soldered to the sample holder plate. The fact that the heat capacity of these remaining parts was a large fraction (about 50°/o) of the
heat capacity with the entire sample in place was deemed to be an advantage in that the temperature drift rate during these second measurements was comparable to that of the previous measurements so that the same proportion of heat capacity of the graphite supports and the electrical leads was taken into account in both cases.
FOOTNOTES

1 See for instance the Proceedings of the Topical Conference on Semimetals, New York, IBM J. Res. Develop. 8, 215 (1964) and the many references quoted there.


7 Ref. 6, p. 321.


9 See Ref. 3, p. A196.


14 L. Onsager, Phys. Rev. 37, 405 (1931); 38, 2265 (1931).
16 See Ref. 5, p. 7.
17 As noted by Long, Ref. 5, the difference between $\lambda''$ and $\lambda$ varied from $6.5\%$ at $4.00^\circ K$ to $2.5\%$ at $1.60^\circ K$.
18 See Ref. 14.
20 See Ref. 13, p. 58.
22 Ref. 19, p. 17.
24 Cominco American, Spokane 4, Washington.
26 S. Cunsolo, et al., Cryogenics 5, 168 (1964).
My thanks to Charles Burlo for the performance of tasks such as this difficult one.

This process consists of producing fine wires by extrusion in molten glass or quartz, later etching away the glass covering with hydrofluoric acid. For more information see H. J. Bomelburg, Rev. Sci. Instr. 30, 1114 (1959).


My own calculations indicate that such a procedure results in less than a 1% error to the true heat capacity over the entire temperature range studied.

This technique was suggested by Dr. C. G. Grenier and seems to be superior to all others used in recent measurements reported in the literature.

See Ref. 17, Section IV.


See Ref. 5, p. 86.

See Ref. 37.

Pure theory suggests the T dependence stated. However, analyses using phenomenological models for the phonon-phonon interaction suggests the isotope resistivity should vary as $T^{1/2}$ which is what is roughly observed. See J. M. Ziman, Theory of Solids (Cambridge University Press, New York, 1964). p. 208.
See Ref. 6, p. 288.

This expression varies from that found by Makinson (see Ref. 8) by a factor of 4/3.


See Ref. 37, p. 481.

See Ref. 38.

See Ref. 3.

See Ref. 6, p.

See Ref. 6, p. 364.


See Ref. 8.

See Ref. 4, p. 215.

See Ref. 38, p. 355.


See Ref. 6, p. 214.


See Ref. 38, p. 354.


See Ref. 13.

See Ref. 5, p. 18.

See Ref. 3, p. A192.

See Ref. 6, p. 107.


See Ref. 62.

See Ref. 4.

See Ref. 10.


M. Bailyn, Phil. Mag. 5, 1059 (1960).


See Ref. 73, pp. 1767-1774.

Earlier determinations of \( n_e \) and \( n_k \) than those cited in Ref. 65 give smaller values. This may account for the low density of states calculated for free electron theory from \( \sum \frac{n_i}{\xi_i} \) by Long (Refs. 3, 4, and 5).

See References 65 and 62.

The density of states when written here with the symbol \( Z_{EF}^{\text{el}} \) to distinguish from the same quantity as measured by transport effects in Section IV and denoted there as \( \Sigma z_{i}^{\text{eff}} \).


80 See Ref. 69, p. 308.


83 D. C. McCollum and B. Taylor, private communication.


86 For instance see Atomic Spectroscopy values, Ref. 85.


88 See Ref. 83.


90 For instance, the values obtained for \( \rho_{11} \) at a given temperature and field were only about half as large as those measured by Long. No accurate values of \( \rho_0 \) were obtained in this experiment for comparison with his.


93 Vacuum Electronics Corporation Mass Spectrometer Leak Detector capable of detecting 1 part in \( 10^7 \) tracer gas (He\(^4\)).

94 He\(^3\) gas was obtained from the Gaseous Isotopes Division, Monsanto Research Corporation, Miamisburg, Ohio. Vapor pressure standard grade gas was used in this experiment. It analysis was
as follows:

more than 99.98\% He$^3$ in total He$^4$

more than 99.9\% total helium

less than 4 \times 10^{-8}\% tritium

Vacuum Electronics Corporation, Throttle Valve R62ST capable of flow rates between 1 atm. cm$^3$ per minute to 3000 atm cm$^3$ per minute.


Texas Instruments Inc., 3609 Buffalo Speedway, Houston, Texas. Name of instrument: Fused Quartz Pressure Gauge.


See Ref. 97, p. 553.

My own calculations using the most pessimistic assumptions for area, emmissivity, etc., give the heat leak due radiation to be less than 1 erg per minute.

See Ref. 5, Appendix.

Emerson and Cummins, No. 2850 GT.


This is a necessary condition in preventing unwanted grounding of the sample in sensitive electrical resistivity measurements.

National Carbon Company, Type N, "Copperclad" projection electrodes were used.

See Ref. 29.

Supplement 1.

Computer Measurements Corporation, Model 226A Universal Counter-Timer.
VITA

Robert Sewall Blewer was born in Shreveport, Louisiana on September 10, 1939. He was graduated from Byrd High School in the same city in 1957, whereupon he enrolled in Louisiana State University. In 1961 he received his Bachelor of Science degree in Physics, and subsequently enrolled in the Graduate Division of the same institution. He has been elected to Phi Eta Sigma, Phi Kappa Phi, and Sigma Pi Sigma scholastic honorary societies. He was married to the former Martha Allison Moseley on August 3, 1963. In 1965 he received his Master of Science degree and is at present a candidate for the degree of Doctor of Philosophy in the Department of Physics and Astronomy of Louisiana State University.
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Candidate: Robert Sewall Blewer

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Title of Thesis: Low Temperature Study of the Electronic Density of States of Antimony.

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Date of Examination:

August 11, 1966