ILLINOIS INSTITUTE OF TECHNOLOGY

MASTER

MAGNETO-THERMAL CONDUCTIVITY OF PYROLYTIC
GRAPHITE BETWEEN 0.36°K and 4.2°K

BY

SHUI YING LU

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Physics
in the Graduate School of
Illinois Institute of Technology

Approved

Chen-Kin Chan
Adviser

CHICAGO, ILLINOIS
December, 1970

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

129

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

The basal plane thermal conductivity of two highly oriented pyrolytic samples was measured in the temperature region between 0.36 to 4.2°K in various magnetic fields up to 23 kilogauss. Analysis shows that the measured thermal conductivity is simply the sum of the electronic and lattice contributions.

According to the results, the lattice thermal conductivity does not depend on the external magnetic field. The phonon mean free path is limited only by the crystallite boundaries. This evidence suggests that the electron-phonon interaction is very weak. Both magnitude and temperature dependences of the lattice thermal conductivity can be explained by Komatsu's semi-continuum model.

The electronic thermal conductivity has a strong magnetic field dependence and is proportional to the absolute temperature. It can be related to the electrical conductivity.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	v
LIST OF TABLES	vi
LIST OF FIGURES	vii
CHAPTER	
I. INTRODUCTION	1
Background	
Some previous Basal Plane Thermal Conductivity Measurements	
Some Previous Basal Plane Electrical Conductivity Measurements	
Purpose of This Experiment	
II. THEORY	9
Crystallography and Lattice Model	
Crystallography	
Lattice Model	
Lattice Thermal Conductivity	
Isotope Scattering	
Phonon-phonon Scattering	
Phonon-Electron Scattering	
Crystal Boundaries	
Lattice Specific Heat and Basal Plane Thermal Conductivity Under the Semicontinuum Model	
Electronic Thermal Conductivity	
III. APPARATUS AND EXPERIMENTAL RESULTS	19
Apparatus and Samples	
Experimental Results	
IV. ANALYSIS AND DISCUSSION	23
Separation of Phonon and Electron Thermal Conductivity	
Estimation of Phonon Mean Free Path	

TABLE OF CONTENTS (cont.)

Temperature Dependence of K_L

V. CONCLUSIONS.....	30
APPENDIX	31
BIBLIOGRAPHY	50

ACKNOWLEDGEMENTS

The author wishes to express her deep appreciation to Dr. H. Weinstock for sponsoring this research, for making available the resources of his laboratory; to her thesis Advisor Dr. C. K. Chau for his helpful suggestions and discussions, for his help concerning the experimental aspects of low temperature work.

The financial support for this project is provided by the Atomic Energy Commission which is also gratefully appreciated.

LIST OF TABLES

Table	Page
I. Structural Characteristics of Pyrolytic Graphite Materials.	2
II. Physical Constants for The Graphite Lattice Used in Thermal Conductivity Calculation.	13
III. $\delta(H)$'s Values and Deduced Electrical Resistivity Values by Using Free Electron Lorenz Number.	27

LIST OF FIGURES

Figure		Page
1.	L_a values as a function of heat treatment temperature.	3
2.	Low temperature thermal conductivity measurements.	4
3.	Basal plane electrical resistivity of Pyrolytic graphite after various treatments.	6
4.	Electrical Resistivity in the basal plane direction.	8
5.	Structure of the hexagonal form of graphite.	10
6.	Schematic arrangement of crystalline in polycrystalline graphite.	11
7.	Magneto-thermal conductivity of sample # 1.	21
8.	Magneto-thermal conductivity of sample # 2.	22
9.	Comparison between $K(H_1) - K(H_2)$ and $(\gamma(H_1) - \gamma(H_2))T$ for sample # 1.	25
10.	Comparison between $K(H_1) - K(H_2)$ and $(\gamma(H_1) - \gamma(H_2))T$ for sample # 2.	26

CHAPTER I INTRODUCTION

Background

In recent years it has become feasible to produce massive deposits of pyrolytic graphite through thermal decomposition of a carbon bearing gas on a refractory substrate at temperatures on the order of 2000°C. Furthermore, boron alloying of pyrolytic graphite can now be achieved in a homogeneous manner over a broad range of concentration. Pyrolytic graphite (PG) and its boron alloys (PGB) are polycrystalline solids, but their texture exhibits a high degree of preferred orientation. The basal planes of each crystallite consist of hexagonally arrayed carbon atoms that tend to align themselves parallel to the deposition surface. The individual crystallites assemble into polygonal zones or grains connected by tilt boundaries, thus giving rise to "wrinkled sheets", which are packed to almost the value for the density of a single crystal. To some extent, the preferred orientation transfers the intrinsic crystallite anisotropy to the bulk properties of PG and PGB. These materials can, therefore, be used with advantage to investigate layer-plane as well as c-direction transport phenomena in graphite. On the basis of their morphological characteristics, pyrolytic graphites fall into three main categories whose structural features are summarized in Table I. As indicated by X-ray analysis, these structures--turbostratic, graphitized, and boronated PG--deviate from the single crystal pattern in terms of interlayer spacing, crystallite size, and c-axis alignment.

Heat treated PG undergoes a drastic transformation in its crys-

tal structure, resulting in a much enhanced preferred orientation, accompanied by permanent crystallite growth and progressive layer ordering. The degree of advancement of this transformation depends upon the post deposition treatment: graphitization is initiated by heating to 2500°C and is practically completed after exposure to temperatures in excess of 3500°C. At this stage the layer-plane properties of PG approximate those attributed to the basal planes of single crystalline graphite. The crystallite size and heat treatment temperature relation are shown in Fig. 1.

Table I. Structural Characteristics
of Pyrolytic Graphite Materials.

Structure (grade)	Layer spacing (Å)	Crystallite size (Å)	Average tilt (deg)
Turbostratic (as deposited)	3.42	250	20
Graphitized (heat treated)	3.36	>1000	<5
Boronated (B/C $\leq 1 \times 10^{-2}$)	3.40	300	20

Some Previous Basal Plane Thermal Conductivity Measurements

The basal plane thermal conductivity curve as a function temperature for polycrystalline graphite has a maximum around 100°K. In the temperature region below the maximum, the conductivity can be described as being proportional to some power of the temperature. The magnitude of the conductivity and its temperature dependence for a specimen depends on the crystallite size. The results for three highly oriented graphite samples are shown in Fig. 2 for comparison. Smith and Rasor's Canadian natural graphite²⁸ is shown as curve A. The

Fig. 1. La values as a function of heat treatment temperature.

Fig. 2. Low temperature thermal conductivity measurements.

crystallite size of this sample was estimated visually to be about 100 microns. The other curves are for two highly oriented pyrolytic graphite samples which were deposited at a temperature exceeding 2000°C with a different post-deposition annealing condition. The deposition planes of these specimens are essentially parallel to the basal planes of the crystallites. De Combarieu² annealed his crystal at 2800°C under 200 bars pressure along the direction of the deposition plane. The crystallite size was estimated to be about 25 microns. The results are shown as curve B. Holland, Klein and Straub³ heat-treated their crystal at 3250°C in an inert gas atmosphere, and the crystallite size was estimated to be about 5 microns. The results are shown as curve C. The magnitudes of these thermal conductivities are clearly proportional to their respective crystallite sizes. Their temperature dependence ranges from $T^{1.8}$ for the Canadian natural graphite to $T^{2.7}$ for Holland's sample.

Slack⁴ has summarized much of the work on the well oriented pyrolytic graphite and natural graphite of lower degree of graphitization. In general, the conductivity at temperatures below the conductivity maximum has temperature dependence between $T^{2.4}$ and $T^{2.8}$, with magnitudes approximately one hundredth those of the previously mentioned highly oriented crystals.

Some Previous Basal Plane Electrical Conductivity Measurements

The temperature dependent basal plane electrical resistivity of pyrolytic graphite as a function of heat treatment temperature was measured by C. A. Klein^{1,5}, and the results are summarized in Fig. 3. These curves clearly show that high temperature heat treatment can greatly reduce resistivity. C. A. Klein and M. G. Holland⁶ measured

Fig. 3. Basal plane resistivity of pyrolytic graphite after various treatments.

the electrical resistivity of turbostratic pyrolytic graphite from 1.7°K to 300°K. The resistance is insensitive to temperature below 30°K. This phenomenon suggests that the crystallite boundaries limit the electron mean free path. M. G. Holland, C. A. Klein and W. D. Straub⁷ measured the basal plane electrical conductivity of pyrolytic graphite in the presence of external magnetic fields along the c-axis. The resulting magnetoresistances are shown in Fig. 4.

Purpose of This Experiment

Phonons and electrons both are important heat carriers for graphite in the temperature region below 10°K. The purpose of this experiment is to study the strength of the electron-phonon interaction and to separate the electronic and phonon contributions to the thermal conductivity. The information deduced is needed for the subsequent investigation of phonon scattering by fast neutron induced defects in graphite. In this work, the basal plane thermal conductivity of graphite as a function of temperature from 0.36°K to 4.2°K has been measured in the presence of external magnetic fields along the direction of heat flow. Holland et al.⁷ has done similar work, but with magnetic fields along the c-axis.

Fig. 4. Electrical resistivity in the basal plane direction.

CHAPTER II THEORY

Crystallography and Lattice Model

Crystallography. X-ray investigation shows that a graphite crystal has symmetry $D_h^{6_2}$. The atoms are found to be arranged in parallel layers. The distance between the layers has been reported as $3.354 \text{ \AA}$ at room temperature. In each layer, the carbon atoms form a network of regular hexagons, with a nearest neighbor distance of $1.415 \text{ \AA}$. Ideally the carbon atoms in each layer lie directly in line with the centers of the regular hexagons in the immediately adjacent layers as shown in Fig. 5. This forms a packing sequence ababab . . . , and gives a theoretical density of 2.265 gm/c.c.

In the polycrystalline graphite the individual crystallites are connected by the tilt boundaries as shown in Fig. 6⁸. The average tilt angle can be reduced by high temperature heat treatment. The basal planes of the crystallites in our samples are essentially in perfect alignment.

According to symmetry, and ideal graphite crystal possesses two principal directions: parallel to the hexagonal axis (c-axis); perpendicular to the hexagonal axis (a-axis). We will denote the two principal conductivities by K_c and K_a , respectively. The carbon atoms within each layer strongly couple to each other. Therefore, the magnitude of K_a should be much larger than K_c .

Lattice Model. In order to evaluate the lattice thermal conductivity one

Fig. 5. Structure of the hexagonal form of graphite.

Fig. 6. Schematic arrangement of crystallites in polycrystalline graphite.

needs a lattice model for the phonon spectrum. Komatsu^{9,10} and Nagamiya¹⁰ have proposed a "semi-continuum" model. This model is based on the tight binding within each layer and weak binding between layers. The lattice vibrations can be regarded to be of two approximately independent types: in-plane modes and out-of-plane modes. The in-plane modes are the two dimensional atomic vibrations of each layer and the relative motion of the layers parallel to the basal plane. The out-of-plane modes are the relative motions of the layers along the c-axis. In the long wave length limit, the in-plane modes depend on the elastic constants c_{11} , c_{12} , and c_{44} , while the out-of-plane modes depend on the elastic constants c_{33} and c_{44} . According to this "semi-continuum" model, the average group velocities of phonons for each mode along the a-axis can be expressed as

$$\begin{aligned}\langle v_1 \rangle_a &= \left(\frac{3\pi}{32} \right) \left(\frac{c_{11}}{\rho} \right)^{\frac{1}{2}} = \left(\frac{3\pi}{32} \right) v_L, \\ \langle v_2 \rangle_a &= \left(\frac{3\pi}{32} \right) \left[\frac{1}{2} (c_{11} - c_{12}) / \rho \right]^{\frac{1}{2}} = \frac{3\pi}{32} v_T, \\ \langle v_3 \rangle_a &= \left(\frac{c_{33}}{\rho} \right)^{\frac{1}{2}} \left(\frac{1}{8} \right) \left[1 + \frac{c_{44}}{c_{33}} \ln \left(\frac{c_{33}}{c_{44}} \right)^* \right],\end{aligned}\tag{1}$$

where ρ is the density. The numerical values of the elastic constants and density can be obtained from Table II. Thus at very low temperature ($\leq 4^\circ\text{K}$) the group velocities are constants.

Lattice Thermal Conductivity

The lattice thermal conductivity can be expressed approximately as

$$K \propto \ell v C(T)\tag{2}$$

Table II. Physical Constants for The Graphite Lattice
Used in Thermal Conductivity Calculations.

<hr/>	
(a) Elastic Constants	dynes/cm ² (Komatsu (5))
c_{11}	90.5×10^{11}
c_{12}	22.5×10^{11}
c_{33}	3.56×10^{11}
c_{44}	$(0.07 -- 0.45) \times 10^{11}$
(b) Other Parameter	
ρ	2.26 g/cm^{-3}
(c) Derived parameters using these values and Komatsu's elastic constants	
v_L	$2.01 \times 10^6 \text{ cm sec}^{-1}$
v_T	$1.23 \times 10^6 \text{ cm sec}^{-1}$
(d) Calculated specific heat using Komatsu's model at $T = 4^\circ\text{K}$	
Specific Heat	$\mu\text{J/cm}^\circ\text{K}$
$C_1 + C_2$	91
C_3	415
<hr/>	

where ℓ is the total phonon mean free path, v is the group velocity and $C(T)$ is the specific heat. In a perfect single crystal of graphite there are four major phonon scattering mechanisms: isotopes, anharmonicity, conduction electrons and crystal boundaries.

Isotope Scattering. The natural isotope composition of carbon is 98.89% of ^{12}C and 1.11% of ^{13}C . The work of Ziman¹¹, Berman et al.¹², Klemens¹³, Dreyfus and Maynard¹⁴, and Carruthers¹⁰ lead to the conclusion that the basal plane relaxation rate is proportional to the third power of the wave vector. This scattering mechanism is not important in the temperature region below 10°K.

Phonon-Phonon Scattering. The anharmonicity of the lattice produces phonon-phonon interactions. The three phonon Umklapp processes are the major source of thermal resistance due to these interactions. According to Peierls's theory, the phonon mean free path ℓ_{pp} can be expressed as

$$\ell_{pp} \propto \exp \frac{\Theta}{bT}$$

(3)

where Θ is the Debye temperature and b is on the order of 2. Taylor¹⁶ and Dreyfus and Maynard¹⁴ found that this effect is important at temperatures well above 100°K.

Phonon-Electron Interaction. The finite overlap of conduction band and valence band in graphitized pyrolytic graphite gives rise to semimetallic property of this polycrystalline crystal. However, the relatively small charge carrier densities ($\sim 10^{-4}$ to $10^{-5}/\text{atom}$)⁷

suggests that the scattering of phonons by electrons will be much less important than in metals.

Crystal Boundaries. Below the conductivity maximum, the crystal boundaries limit the phonon mean free path. One can express ℓ approximately equal to the crystal size ℓ_b ,

$$\frac{1}{\ell} = \frac{1}{\ell_i} + \frac{1}{\ell_{pp}} + \frac{1}{\ell_{pe}} + \frac{1}{\ell_b} \approx \frac{1}{\ell_b} \quad (4)$$

Thus, the temperature dependence of lattice thermal conductivity is proportional to the temperature dependence of lattice specific heat,

$$K(T) \propto C(T) \quad (5)$$

Lattice Specific Heat and Basal Plane Thermal Conductivity Under the Semicontinuum Model

According to the semicontinuum model, the theoretical derivation of specific heat by Komatsu^{9,10} and Nagamiya¹⁰ can be summarized as

$$\begin{aligned} C_{1,2} &\propto T^2 & 25^\circ\text{K} < T < 192^\circ\text{K}, \\ C_{1,2} &\propto T^3 & T \ll 25^\circ\text{K}, \\ C_3 &\propto T^2 & 2^\circ\text{K} < T < 192^\circ\text{K}, \\ C_3 &\propto T^3 & T \ll 2^\circ\text{K}, \end{aligned} \quad (6)$$

where C_1 and C_2 are the specific heats contributed by the in-plane

longitudinal and transverse modes respectively, and C_3 is due to the out-of-plane mode.

Specific heat measurements below 20°K reported by De Sorbo¹⁸, Van De Hoven¹⁹ and other authors^{15, 20, 21, 22} show a transition from T^2 to T^3 dependence below 10°K and the T^3 dependence occurs below 1°K. The specific heats measured at 4°K varies approximately from 60 to 400 $\frac{\mu J}{^\circ K cm^3}$, and the transition temperature (from T^2 to T^3 dependence) depends on the degree of perfection of the sample. Therefore, Komatsu's model appears to explain the specific heat measurements satisfactorily.

According to Komatsu's model, the basal plane thermal conductivity below the conductivity maximum can be expressed as

$$K_a = L_a \sum_p \langle v_p \rangle_a C_p, \quad (7)$$

where C_p is given by eq. (6), $\langle v_p \rangle_a$ by eq. (1) and L_a is the crystallite size along the basal plane. Numerical values for C_p are in Table II.

Electronic Thermal Conductivity

The band structure of perfect graphite has been investigated in recent years²³. A small interaction between second-nearest planes gives rise to a certain amount of band overlap at the Fermi energy, thus generating positive and negative carriers that are closely balanced in concentration. These free carrier densities are low (about 10^{-4} /atom at room temperature) leading to essentially semi-metallic characteristics. In fact, an analysis of PG layer-plane properties can be based on a simple two-band model (STB model).

Transport takes place simultaneously in the valence and conduction bands, and the carriers must be treated exactly by means of Fermi-Dirac statistics. Following the treatment of Goldsmid²⁴, carrier scattering can be represented by a relaxation time τ which is taken to be of the form

$$\tau = \tau_0 E^s \quad (8)$$

where τ_0 is a function of temperature only, and E is the electron energy. For lattice scattering $s = -\frac{1}{2}$ and $\tau_0 \propto \frac{1}{T}$; for ionized impurities $s = \frac{3}{2}$ and τ_0 does not depend on temperature explicitly. The ratio of the electronic thermal conductivity to electrical conductivity is

$$\frac{\kappa_E}{\sigma T} = \frac{k_B^2}{e^2} \left\{ \frac{(s + \frac{7}{2})(s + \frac{3}{2}) F_{(s + \frac{5}{2})}(\eta) F_{(s + \frac{1}{2})}(\eta) - (s + \frac{5}{2})^2 F_{(s + \frac{3}{2})}^2(\eta)}{(s + \frac{3}{2})^2 F_{(s + \frac{1}{2})}(\eta)} \right\} ,$$

where
$$F_r(\eta) = \int_0^\infty \frac{x^r}{1 + e^{x-\eta}} dx ,$$

$$\eta = \frac{\bar{\mu}}{k_B T} \quad (9)$$

$\bar{\mu}$ is the Fermi energy.

For highly oriented pyrolytic graphite the energy overlap, E_0 , of the band structure is believed to have a value around 0.028 eV³. In liquid helium temperature the Fermi level is "frozen" halfway between the bottom of the conduction band and the top of the valence band.

For $T \leq 4^\circ \text{K}$

$$\eta = \frac{E_0}{2k_B T} \geq \frac{2.8 \times 10^{-2}}{1.38 \times 10^{-3}} \approx 20 \quad (10)$$

Thus, there is a highly degenerate system throughout the temperature range of interest ($\leq 4^\circ \text{K}$). In this temperature limit, the η is large, and the Fermi-Dirac integral can be expressed as a series of descending powers of η in the form

$$F_r(\eta) = \frac{\eta^{r+1}}{r+1} + r\eta^{r-1} \frac{\pi}{6} + r(r-1)(r-2)\eta^{r-3} \frac{7\pi^4}{360} + \dots \quad (11)$$

The terms of this series converge rapidly for large values of η .

As a result, eq. 9 can be simplified into the following form:

$$\frac{K_E}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = L_0 \quad (12)$$

where L_0 is the free electron Lorenz number, independent of s and η .

CHAPTER III APPARATUS AND EXPERIMENTAL RESULTS

Apparatus and Samples

The basal plane thermal conductivity of pyrolytic graphite has been measured as a function of temperature from 0.36°K to 4.2°K and as a function of magnetic field up to 23kG.

The ^3He refrigerator used in this experiment was built by Dr. C. C. Ni. A description of the detailed construction and operation of this apparatus, as well as the thermal conductivity measurement technique, may be found elsewhere²⁵.

The two pyrolytic graphite samples were hot pressed at temperatures above 3000°C. The dimensions are 1.34 in x 0.226 in x 0.0656 in and 0.95 in x 0.227 in x 0.0737 in for samples # 1 and # 2, respectively. The samples are very pure and highly oriented graphite. The degree of graphitization is higher than 98%⁵. Under a microscope, the crystallite size is estimated to be about 100 microns.

Experimental Results

The temperature dependence of the basal plane thermal conductivity of these two samples for various magnetic fields along the basal plane is presented in Fig. 7 and Fig. 8. All data points are listed in the Appendix. For both samples, the thermal conductivity as a function of temperature decreases with increasing magnetic field. It is observed that the higher the magnetic field, the higher becomes the temperature dependence of the conductivity, especially below 1°K. The zero field thermal conductivity at 4°K for both samples is

$1.5 \times 10^{-1} \frac{\text{watt}}{\text{cm}^{\circ}\text{K}}$. The thermal conductivity of sample # 1 with magnetic field 23.1 kG exhibits a $T^{2.6}$ dependence for $T > 1^{\circ}\text{K}$, and the conductivity of sample # 2 has a $T^{2.7}$ dependence with a magnetic field of 20.4 kG. These temperature dependences and thermal conductivity magnitude bear close resemblance to de Combarieu's result (see Fig. 2), which is reasonable considering the similarity between our samples.

Fig. 7. Magneto-thermal conductivity of sample # 1.

Fig. 8. Magneto-thermal conductivity of sample # 2.

CHAPTER IV ANALYSIS AND DISCUSSION

Separation of Phonon and Electron Thermal Conductivity

At temperature below 10°K electrons and phonons both contribute to the heat transport along the basal plane in graphite. Assuming the electron-phonon interaction is not important, total thermal conductivity may be expressed as the sum of the phonon and electron components,

$$K = K_L + K_E \quad (13)$$

Furthermore, it is assumed that the electron gas is degenerate in the samples measured. Thus, the electronic thermal conductivity is expressed by eq.(12)

$$K_E = \gamma(H)T = L_0 \sigma T \quad (12)$$

Below 4°K, σ is independent of temperature. Thus the electronic thermal conductivity is proportional to T.

In the presence of a magnetic field along the basal plane the thermal conductivity is

$$K(H) = K_L + K_E(H) = AT^n + \gamma(H)T \quad (14)$$

where AT^n represents the phonon component. Eq. (16) can be rewritten as

$$\frac{K(H)}{T} = AT^{n-1} + \gamma(H) \quad (15)$$

By extrapolating the curves of $\frac{K(H)}{T}$ vs T for different magnetic

fields, we can obtain $\gamma(H)$. The $\gamma(H)$ values for both samples under magnetic fields and deduced values of electrical resistivity using the free electron Lorenz number are listed in Table III.

The difference between two thermal conductivities corresponding to two magnetic fields, $K(H_1) - K(H_2)$, is plotted as a function of temperature as shown in Fig. 9 and Fig. 10 for sample # 1 and sample # 2, respectively. The function $[\gamma(H_1) - \gamma(H_2)] T$ is also plotted in the above figure for comparison. The agreement within the error ($\pm 5\%$) between these two plots indicates that the difference between the thermal conductivities indeed can be simply represented by the difference between electronic thermal conductivities, i.e. $K_E(H_1) - K_E(H_2)$. Thus the independence of magnetic field of the phonon thermal conductivity is justified. And the separation of phonon and electron thermal conductivity is shown to be feasible. Furthermore, the electronic component is proportional to the temperature. The relation between the proportional constant $\gamma(H)$ and the electrical conductivity $\sigma(H)$ may be revealed by further electrical conductivity measurement. For a perfect graphite, the free electron Lorenz number L_0 is expected to play the role.

Estimations of Phonon Mean Free Path

According to eq. 7, the lattice thermal conductivity is

$$K_a = L_a (\langle v_1 \rangle_a C_1 + \langle v_2 \rangle_a C_2 + \langle v_3 \rangle_a C_3) \quad (15)$$

Fig. 9. Comparison between $K(H_1) - K(H_2)$ and $(\gamma(H_1) - \gamma(H_2))T$ for sample # 1.

Fig. 10. Comparison between $K(H_1) - K(H_2)$ and $(\gamma H_1 - \gamma(H_2))T$ for sample # 2.

Table III. $\gamma(H)$'s Values and Deduced Electrical Resistivity Values by Using Free Electron Lorenz Number.

H (kG)	$\gamma \left(\frac{v^2}{^\circ K \Omega \text{ cm}} \right)$	$\rho \left(\Omega \text{ cm} \right)$
Sample # 1		
0	9.2×10^{-3}	2.7×10^{-6}
5.6	2.8×10^{-3}	8.8×10^{-6}
23.1	5.0×10^{-4}	4.9×10^{-5}
Sample # 2		
0	9.2×10^{-3}	2.7×10^{-6}
2.1	2.4×10^{-3}	1.0×10^{-5}
10.1	3.0×10^{-4}	8.2×10^{-5}
20.4	8.0×10^{-5}	3.1×10^{-4}

Komatsu's theoretical values for C_p and $\langle v_p \rangle_a$ at 4°K are (see Table II)

$$\begin{aligned} C_1 + C_2 &= 86.5 \frac{\mu J}{cm^3 \circ K}, \\ \langle v_1 \rangle_a &= 5.9 \times 10^5 \text{ cm/sec}, \\ \langle v_2 \rangle_a &= 3.6 \times 10^5 \text{ cm/sec}, \\ \langle v_3 \rangle_a &= (5.53 \times 10^4 - 7.18 \times 10^4) \text{ cm/sec} . \quad (16) \end{aligned}$$

The thermal conductivity of both samples at 4°K is $1.5 \times 10^{-1} \frac{\text{watt}}{\text{cm} \circ K}$.

Substituting the above numerical values into eq. 18 one deduces that

L_a is

$$L_a = (2.2 \times 10^5 - 2.4 \times 10^5) \text{ \AA} . \quad (17)$$

The above estimated crystallite size of our samples along basal plane is in reasonable agreement with the data presented in Fig. 1. And its value is very close to de Combarieu's crystal.

Temperature Dependence of K_L

From the feasibility of separation of phonon and electronic thermal conductivity in Sec. A of this chapter, one can obtain K_L by subtracting the electronic component from the total thermal conductivity. The results are presented in Fig. 7 and Fig. 8, denoted as "phonon-only". The phonon thermal conductivity has temperature dependence T^n with $n = 3$ for $T < 1^\circ K$, $n = 2.6$ and 2.7 between $1^\circ K$ and $4^\circ K$ for sample # 1 and sample # 2, respectively. These results agree with de Combarieu's experimental data with zero magnetic field. For his case the thermal conductivity was measured above $5^\circ K$. In that tem-

perature range the phonon component predominates the electronic component (although below 10°K the electronic component presents).

Therefore the comparison between the phonon thermal conductivity of present work and de Combarieu's thermal conductivity measurement is reasonable. Below 1°K the T^3 dependence indicates the strong evidence that phonon thermal conductivity is proportional to the lattice specific heat in agreement with Komatsu's model.

CHAPTER V CONCLUSIONS

The basal plane thermal conductivity with magnetic field along the a-axis has been measured between 0.36°K and 4.2°K. The conclusions are as follows:

Firstly, the thermal conductivity of graphite at very low temperature ($\leq 4^\circ\text{K}$) can be written as the sum of two independent components: phonon thermal conductivity; electronic thermal conductivity.

Secondly, the phonon thermal conductivity is independent of the magnetic field. The temperature dependence T^n agrees with Komatsu's theoretical prediction.

Thirdly, the crystallite size is estimated to be about $2 \times 10^5 \text{ \AA}$ in qualitative agreement with heat treatment study, and very close to that of de Combariou's sample $2.5 \times 10^5 \text{ \AA}$.

Fourthly, the electronic thermal conductivity is proportional to temperature. The proportional constant is related to the electrical conductivity.

Lastly, further investigation of electrical conductivity may provide us a positive check on the STB model in pyrolytic graphite.

APPENDIX

Sample # 1 H = 0

Temperature (°K)	Thermal Conductivity (watts/cm°K)
0.369	0.00300
0.381	0.00314
0.394	0.00327
0.406	0.00341
0.418	0.00368
0.438	0.00379
0.442	0.00381
0.455	0.00405
0.470	0.00421
0.480	0.00431
0.497	0.00469
0.509	0.00469
0.527	0.00493
0.536	0.00509
0.540	0.00506
0.550	0.00523
0.562	0.00533
0.566	0.00548
0.584	0.00562
0.614	0.00594
0.630	0.00613
0.651	0.00639
0.675	0.00689
0.697	0.00697
0.736	0.00746
0.762	0.00780
0.791	0.00822

Sample # 1 H = O (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
0.823	0.00853
0.825	0.00893
0.877	0.00919
0.910	0.00959
0.933	0.00994
0.984	0.0106
1.018	0.0118
1.093	0.0131
1.178	0.0166
1.182	0.0157
1.188	0.0168
1.203	0.0171
1.207	0.0175
1.219	0.0176
1.238	0.0179
1.261	0.0185
1.286	0.0191
1.291	0.0196
1.319	0.0199
1.356	0.0209
1.393	0.0218
1.401	0.0231
1.505	0.0254
1.591	0.0284
1.657	0.0301
1.773	0.0346
1.780	0.0345
1.869	0.0379
1.895	0.0392

Sample # 1 H = 0 (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
2.001	0.0427
2.162	0.0493
2.286	0.0523
2.313	0.0558
2.325	0.0578
2.382	0.0571
2.469	0.0640
2.493	0.0618
2.532	0.0666
2.596	0.0680
2.673	0.0696
2.698	0.0752
2.716	0.0721
2.742	0.0758
2.758	0.0773
2.794	0.0775
2.921	0.0866
2.960	0.0851
2.967	0.0899
3.010	0.0908
3.143	0.100
3.149	0.0977
3.187	0.101
3.222	0.104
3.289	0.108
3.308	0.109
3.429	0.116
3.440	0.119
3.457	0.119

Sample # 1 H = O (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
3.583	0.127
3.634	0.131
3.731	0.140
3.829	0.146
4.090	0.167
4.189	0.178

Sample # 1 $H = 5.6\text{kG}$

Temperature (°K)	Thermal Conductivity (watts/cm°K)
0.417	0.00132
0.433	0.00138
0.446	0.00140
0.466	0.00146
0.497	0.00157
0.521	0.00166
0.555	0.00182
0.587	0.00201
0.593	0.00205
0.622	0.00226
0.630	0.00229
0.647	0.00231
0.669	0.00239
0.691	0.00244
0.722	0.00274
0.761	0.00302
0.781	0.00314
0.817	0.00341
0.842	0.00355
0.890	0.00377
0.904	0.00409
0.958	0.00421
1.043	0.00450
1.214	0.00741
1.253	0.00795
1.313	0.00894
1.356	0.0097
1.400	0.0106
1.459	0.0118

Sample # 1 H = O (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
1.521	0.0129
1.601	0.0152
1.713	0.0185
1.802	0.0205
1.910	0.0240
2.104	0.0285
2.172	0.0318
2.236	0.0340
2.281	0.0359
2.359	0.0385
2.432	0.0417
2.558	0.0472
2.649	0.0514
2.791	0.0581
2.990	0.0686
3.169	0.0783
3.309	0.0866
3.445	0.0944
3.558	0.104
3.753	0.115
4.008	0.134
4.227	0.156

Sample # 1 H = 23.1kG

Temperature (°K)	Thermal Conductivity (watts/cm°K)
0.366	0.000252
0.392	0.000292
0.405	0.000318
0.419	0.000355
0.433	0.000376
0.448	0.000397
0.472	0.000441
0.488	0.000475
0.509	0.000517
0.532	0.000587
0.555	0.000632
0.574	0.000678
0.588	0.000713
0.617	0.000797
0.636	0.000847
0.655	0.000899
0.677	0.000964
0.693	0.00402
0.751	0.00116
0.775	0.00128
0.800	0.00142
0.826	0.00148
0.848	0.00163
0.876	0.00179
0.896	0.00190
0.927	0.00210
0.945	0.00221
0.969	0.00240
0.989	0.00254

Sample # 1 H = 23.1kG (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
1.012	0.002745
1.029	0.00288
1.053	0.00308
1.070	0.00324
1.088	0.00342
1.125	0.00381
1.145	0.00401
1.162	0.00423
1.182	0.00443
1.216	0.00489
1.244	0.00505
1.319	0.00612
1.364	0.00694
1.424	0.00794
1.484	0.00919
1.533	0.0105
1.567	0.0107
1.662	0.0130
1.680	0.0135
1.720	0.0143
1.789	0.0163
1.892	0.0187
1.987	0.0215
2.013	0.0224
2.073	0.0245
2.090	0.0248
2.186	0.0280
2.215	0.0290
2.305	0.0319

Sample # 1 H = 23.1kG (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
2.311	0.0329
2.408	0.0346
2.528	0.0395
2.607	0.0436
2.664	0.0450
2.837	0.0537
2.887	0.0550
2.964	0.0586
3.093	0.0662
3.133	0.0671
3.309	0.0762
3.340	0.0793
3.480	0.0861
3.594	0.0932
3.647	0.0958

Sample # 2 H = 0

Temperature (°K)	Thermal Conductivity (watts/cm°K)
0.383	0.00317
0.399	0.00333
0.414	0.00352
0.420	0.00358
0.429	0.00371
0.440	0.00385
0.449	0.00397
0.454	0.00402
0.466	0.00418
0.475	0.00427
0.500	0.00457
0.536	0.00518
0.574	0.00556
0.589	0.00568
0.612	0.00593
0.638	0.00621
0.662	0.00644
0.682	0.00679
0.703	0.00713
0.723	0.00742
0.725	0.00764
0.744	0.00782
0.766	0.00791
0.784	0.00801
0.788	0.00816
0.810	0.00825
0.831	0.00868
0.856	0.00910
0.877	0.00943
0.897	0.00964

Sample # 2 H = 0 (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
0.926	0.0102
0.927	0.00995
0.946	0.0104
0.971	0.0108
1.009	0.0112
1.104	0.0138
1.134	0.0140
1.179	0.0146
1.222	0.0149
1.485	0.0154
1.569	0.0257
1.634	0.0284
1.685	0.0291
1.747	0.0317
1.764	0.0330
1.776	0.0322
1.817	0.0188
1.843	0.0350
1.914	0.0375
1.983	0.0405
1.988	0.0410
2.055	0.0430
2.128	0.0459
2.261	0.0516
2.297	0.0514
2.430	0.0585
2.516	0.0629
2.593	0.0653
2.647	0.0683

Sample # 2 H = 0 (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
2.712	0.0714
2.789	0.0753
2.904	0.0807
2.918	0.0825
2.968	0.0851
3.037	0.0887
3.101	0.0926
3.136	0.0945
3.183	0.0976
3.223	0.0988
3.330	0.107
3.470	0.114
3.479	0.115
3.604	0.123
3.746	0.133
3.835	0.139
3.975	0.150
4.163	0.164
4.345	0.178

Sample # 2 H = 2.1kG

Temperature (°K)	Thermal Conductivity (watts/cm°K)
0.378	0.000992
0.396	0.00106
0.403	0.00109
0.450	0.00125
0.464	0.00133
0.495	0.00143
0.528	0.00168
0.542	0.00162
0.576	0.00175
0.597	0.00288
0.638	0.00203
0.651	0.00243
0.691	0.00227
0.738	0.00252
0.764	0.00266
0.797	0.00286
0.820	0.00299
0.867	0.00329
0.927	0.00370
0.960	0.00390
1.013	0.00428
1.154	0.00568
1.204	0.00658
1.237	0.00717
1.288	0.00801
1.349	0.00909
1.462	0.0111
1.535	0.0127
1.574	0.0132
1.598	0.0142

Sample # 2 H = 2.1kG (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
1.663	0.0154
1.752	0.0178
1.782	0.0182
1.813	0.0196
1.852	0.0203
1.930	0.0226
1.984	0.0236
2.002	0.0250
2.055	0.0260
2.135	0.0290
2.292	0.0346
2.373	0.0387
2.424	0.0405
2.518	0.0447
2.623	0.0490
2.676	0.0484
2.786	0.0560
2.918	0.0622
2.983	0.0655
3.054	0.0695
3.083	0.0747
3.129	0.0726
3.274	0.0819
3.332	0.0860
3.470	0.1260
3.602	0.112
3.753	0.119
3.896	0.127
4.323	0.162
4.468	0.177

Sample # 2 H = 10.1kG

Temperature (°K)	Thermal Conductivity (watts/cm°K)
0.409	0.00251
0.440	0.000389
0.464	0.000322
0.482	0.00341
0.515	0.000393
0.521	0.000403
0.539	0.000221
0.551	0.000458
0.591	0.000537
0.607	0.000563
0.626	0.000626
0.662	0.000701
0.695	0.000793
0.707	0.000842
0.756	0.000992
0.785	0.00108
0.842	0.00131
0.917	0.00166
0.951	0.00190
0.976	0.00199
1.038	0.00232
1.066	0.00250
1.154	0.00309
1.201	0.00384
1.251	0.00446
1.284	0.00461
1.337	0.00556
1.386	0.00624
1.469	0.00755
1.545	0.00882

Sample # 2 H = 10.1kG (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
1.572	0.00983
1.675	0.0115
1.751	0.0133
1.788	0.0140
1.840	0.0155
1.857	0.0156
1.934	0.0177
1.994	0.0191
2.006	0.0199
2.067	0.0211
2.141	0.0233
2.281	0.0277
2.285	0.0282
2.412	0.0326
2.515	0.0369
2.620	0.0405
2.726	0.0441
2.800	0.0471
2.893	0.0515
2.941	0.0540
2.967	0.0541
3.039	0.0574
3.102	0.0613
3.330	0.0730
3.461	0.0817
3.599	0.0817
3.684	0.0928
3.800	0.1010
3.944	0.109
4.101	0.1220
4.241	0.126

Sample # 2 H = 20.4kG

Temperature (°K)	Thermal Conductivity (watts/cm°K)
0.429	0.000177
0.462	0.000216
0.492	0.000250
0.519	0.000287
0.550	0.000336
0.555	0.000326
0.579	0.000394
0.592	0.000407
0.633	0.000472
0.638	0.000509
0.688	0.000623
0.725	0.000760
0.729	0.000746
0.782	0.000920
0.793	0.000956
0.810	0.00103
0.848	0.00117
0.887	0.00133
0.909	0.00146
0.958	0.00169
0.998	0.00187
1.006	0.00195
1.109	0.00261
1.153	0.00292
1.220	0.00356
1.261	0.00468
1.335	0.00588
1.432	0.00756
1.484	0.00833
1.512	0.00913

Sample # 2 H = 20.4kG (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
1.588	0.00960
1.649	0.0109
1.688	0.01176
1.746	0.0132
1.787	0.0146
1.834	0.0166
1.882	0.0167
1.899	0.0176
1.961	0.0190
2.047	0.0217
2.082	0.0219
2.112	0.0236
2.246	0.0283
2.393	0.0330
2.522	0.0384
2.595	0.0405
2.605	0.0416
2.723	0.0445
2.741	0.0477
2.805	0.0493
2.907	0.0523
2.910	0.0536
2.972	0.0567
3.075	0.0620
3.107	0.0638
3.150	0.0644
3.243	0.0712
3.350	0.0772
3.469	0.0832

Sample # 2 H = 20.4kG (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm°K)
3.480	0.0874
3.606	0.0911
3.740	0.999
4.006	0.119
4.173	0.128
4.310	0.135

BIBLIOGRAPHY

1. Walker, P. L., Chemistry and Physics of Carbon, Vol. 2, p.225. Marcel Dekker, New York (1965).
2. de Combarieu, A. J., de Physique 28, 951 (1967).
3. Holland, M. G. Klein, C. A., and Straub, W. D., J. Phys. Chem. Solids 27, 905 (1966).
4. Slack, G. A., Phys. Rev. 127, 694 (1962).
5. Klein, C.A., Proceedings of The Fifth Conference on Carbon, Vol. 2, p.11. University of Buffalo, New York (1963).
6. Klein, C. A., and Holland, M. G., Phys. Rev. 136, 575 (1964).
7. Bowman, J. C., Krumhansl, J. A., and Meers, J. T., Industrial Carbon and Graphite, 52. Society of Chemical Industry, London (1958).
8. Castle, J. G., Proceedings of the First and Second Conferences on Carbon, p.13. University of Buffalo, New York (1956).
9. Komatsu, K., J. Phys. Soc. Japan 10, 346 (1955); J. Phys. Chem. Solids 6, 380 (1958).
10. Komatsu, K., and Nagamiya, T., J. Phys. Soc. Japan 6, 438 (1951); J. Chem. Phys. 22, 1457 (1954).
11. Carruthers, P. A., Rev. Mod. Phys. 33, 92 (1961).
12. Berman, R., Netleu, P. T., Sheard, F. V., Spencer, A. N., Stevenson, R. W. H., and Ziman, J. M., Proc. Roy. Soc. A 253, 403 (1959).
13. Klemens, P. G., Solid State Physics, Vol. 7, 1. Academic Press, New York (1958).
14. Dreyfus, B., and Maynard, R., J. de Physique 28, 951 (1968).
15. Bergenlid, U., Hill, R. W., Webb, L. T., and Wilks, J., Phil. Mag. 45, 851 (1954).
16. Taylor, R., Phil. Mag. 13, 157 (1966).
17. De Sorbo, W., and Tyler, W. W., J. Chem. Phys. 21, 1660 (1953).
18. De Sorbo, W., and Nichols, G. E., J. Chem. Solids 6, 352 (1958).
19. Van De Hoven, B. J., and Keesom, P. H., Phys. Rev. 130, 1318 (1963).
20. De Sorbo, W., J. Amer. Chem. Soc. 77, 4713 (1955).

21. De Sorbo, W., J. Chem. Phys. 23, 1970 (1955).
22. Keesom, P. H. and Pearlman, N., Phys. Rev. 99, 1119 (1955)
23. Wallace, P. R., Phys. Rev. 71, 622 (1947).
24. Drabble, J. R., and Goldsmid, H. J., Thermal Conduction in Semiconductor, Chapter 4. Oxford, New York, Pergamon Press (1961).
25. Ni, C. C., Ph.D. Thesis, 51 - 60. Illinois Institute of Technology, Chicago (1969).
26. Frechette, V. D., Hay, J., and Tao, Y., Proceedings of The First and Second Conferences on Carbon, p.15. University of Buffalo, New York (1956).
27. Klein, C. A., Straub, W. D., Phys. Rev. 125, 468 (1962).
28. Smith, A. W., and Rasor, H. S., Phys. Rev. 104, 885 (1956).