

Thermal Conductivity, Electrical Resistivity, and Thermoelectric Power of Graphite

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The thermal conductivity, electrical resistivity, and thermoelectric power have been measured in the temperature range from 20°K to 300°K for samples of artificial extruded graphite, natural molded graphite, and lampblack graphite. Experimental results are presented and discussed briefly in relation to theory.

Due to the very large Wiedemann-Franz ratio and its dependence on temperature and type of graphite, thermal conductivity in graphite is attributed primarily to lattice waves. Scattering of lattice waves from crystallite boundaries limits the conductivity through most of the temperature range investigated. Interpretation of the data in terms of the simple Debye equation for lattice conductivity permits rough estimates of effective crystallite size. At low temperatures, the dependence of conductivity on temperature is more rapid than the dependence of heat capacity, in disagreement with the Debye equation.

The temperature dependence of electrical resistivity is interpreted using a modified Wallace zone theory which permits the Fermi level to differ in position from the zone boundary, owing to an excess or deficit of electrons. Scattering of electrons in the temperature range of interest is attributed to crystallite boundaries or atomic imperfections and assumed temperature independent. The temperature dependence of the Fermi level which gives the best fit to experimental data is not in agreement with theoretical predictions.

I. SAMPLES STUDIED

THE four polycrystalline graphite samples studied were in the form of rods three-eighths inch in diameter and three inches long. Samples *A* and *B* are conventional coke base, pitch bonded, extruded graphite with bulk density of about 1.70 g/cm³. The theoretical single crystal density is 2.25 g/cm³. Sample *A* is a National Carbon Company grade CS graphite with axis of the sample perpendicular to the preferred *c*₀ axis orientation. Sample *B* is a National Carbon Company grade AGOT graphite with the sample axis parallel to preferred *c*₀ axis orientation. Sample *C* is natural

graphite base, pitch bonded, and molded, with a bulk density of about 1.80 g/cm³ and with the sample axis perpendicular to the preferred *c*₀ axis orientation. Sample *D* is a lampblack base, pitch bonded, molded graphite with bulk density of about 1.65 g/cm³. The axis of sample *D* is parallel to the preferred *c*₀ axis orientation although because of the small crystallite size, orientation effects are comparatively small for this type of graphite.¹

II. EXPERIMENTAL PROCEDURE

Figure 1 indicates the arrangement used in supporting the specimen and providing suitable thermal conditions during measurements. The container shown is supported in a Dewar containing either liquid hydrogen, liquid nitrogen, solid carbon dioxide and acetone, or ice water, depending on the temperature range desired. The Dewar in turn is contained in a cryostat which may be evacuated to reduce the vapor pressure over the liquid when working with hydrogen or nitrogen. To provide thermal isolation of the sample, the container shown in Fig. 1 is evacuated during measurements to about 5×10^{-6} mm mercury. Alternatively, helium exchange gas may be put in the container to aid thermal equilibration of the specimen and bath.

All heater and thermocouple leads pass through small paraffin filled holes in the copper "thermal sink" and are brought to the bath temperature at this point. Thermocouple leads to the specimen and the specimen heater, and current and potential leads to the specimen heater pass through paraffin filled holes in the "block." Positions of thermocouples are designated by TC in the diagram. TC-5 and TC-6 provide the critical temperature measurements establishing ΔT and the average

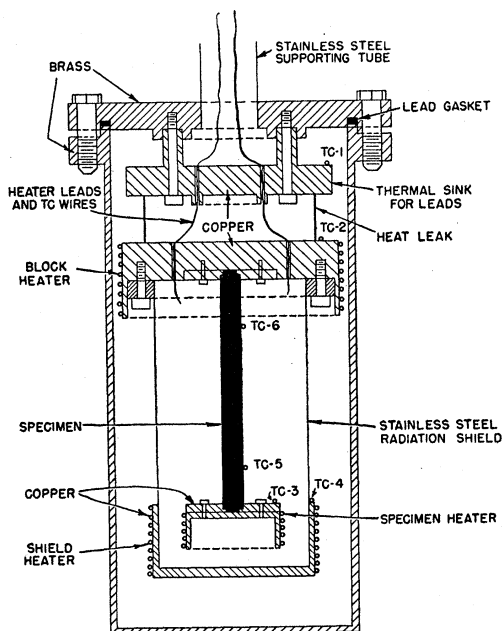


FIG. 1. Diagram of the apparatus.

* The Knolls Atomic Power Laboratory is operated by the General Electric Company for the U. S. Atomic Energy Commission.

¹ For general information related to the preparation and properties of artificial graphites, see C. L. Mantell, *Industrial Carbon* (D. Van Nostrand Company, Inc., New York, 1946), and the review paper by J. P. Howe, *J. Am. Ceram. Soc.* 35, 275 (1952).

temperature of the specimen. For measurements above nitrogen temperature (77°K), TC-3 and TC-4 are held at the same temperature to minimize radiation losses. All of the thermocouples are of copper-constantan, made from stock, samples of which had been calibrated against the Ohio State University temperature scale.² The block heater and heat leak permit measurements in temperature regions between various bath temperatures. This technique has been used extensively by Powers and is described by him³ in greater detail.

All thermoelectric voltages and potential measurements for power and current calculations are made using a Leeds and Northrup White double potentiometer (0–10,000 microvolts) and high sensitivity galvanometer. The scale sensitivity of this system is 3.5 ± 0.1 cm/microvolt. Use of either the copper or constantan elements of TC-5 and TC-6 as potential leads permits electrical resistivity measurements and thermoelectric power measurements of either copper-graphite or constantan-graphite.

To support the samples in the cryostat, copper disks were soldered to the ends of the specimens after copper plating of the graphite. The copper disks were then fastened to the block and heater by screws. The thermocouples TC-5 and TC-6 were soldered to 0.040-in. copper rods which were pressed snugly into holes in the samples.

III. EXPERIMENTAL RESULTS

Figure 2 shows thermal conductivity data for the four samples. Temperature dependent errors are attributable to power loss in the heater and thermocouple leads, thermal drift, radiation loss, the decrease in sensitivity of thermocouples at low temperatures, and deviations of the individual thermocouples from the standard calibration. Of these, the most important is due to lead losses. As the lengths of the leads and the thermal gradients between the block and the termination of the leads are known (TC-2, TC-3), corrections for lead losses are made using data of Powers³ for the thermal conductivity of copper and constantan. This correction may be made fairly accurately for data points taken with the specimen near bath temperature, but not for data points in temperature regions such that a large gradient exists between the sink and the block. Under such conditions, failure to attain equilibrium between the leads and the block results in an under estimation of the gradient in the leads. Data points between 35 and 55°K tend to be somewhat high because of this even for the high conductivity specimens. The uncertainty in the magnitude of conductivity data is estimated to be ± 5 percent for the highest conductivity points and ± 10 percent for the lowest conductivity points.

² Rubin, Johnston, and Altman, *J. Am. Chem. Soc.* **73**, 3401 (1951). We are indebted to W. DeSorbo for providing us with the thermocouple wire and calibration charts.

³ Powers, Schwartz, and Johnston (to be published).

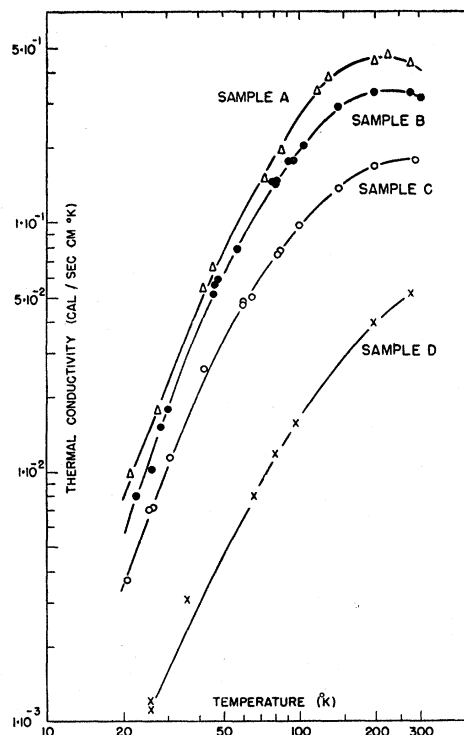


FIG. 2. Thermal conductivity as a function of temperature for the four samples studied.

Our conductivity data for samples A and B agree well with data of Berman⁴ and Rasor⁵ for samples of extruded graphite which are probably similar to our samples. Our data do not agree with data of Buerschaper⁶ which indicate that the conductivity of graphite continues to increase as the temperature decreases down to 90°K.

Figure 3 shows the electrical resistivity data for specimens A, B, and C. Figure 4 compares the higher resistivity lampblack graphite with sample B. The data are probably accurate to ± 0.5 percent except for a temperature independent, geometric error of at most 2 percent. The temperature dependence of the resistivity of samples A and B agrees fairly well with work of Goetz and Holser⁷ for similar type graphite. The resistivity of the lampblack graphite sample may be represented quite accurately by

$$\rho = A - BT, \quad (1)$$

where A is 7.75×10^{-3} ohm-cm and B is 7.43×10^{-6} ohm-cm/deg. Sample C has a resistivity comparable

⁴ R. Berman, *Phys. Rev.* **76**, 315 (1949); (to be published). We are indebted to Dr. Berman for sending us experimental data prior to publication and for helpful discussion related to the theory of lattice conduction.

⁵ N. S. Rasor (unpublished data). We are indebted to W. P. Eatherly for informing us of this recent work at North American Aviation Company.

⁶ R. A. Buerschaper, *J. Appl. Phys.* **15**, 452 (1944).

⁷ A. Goetz and A. Holser, *Trans. Electrochem. Soc.* **82**, 391 (1942).

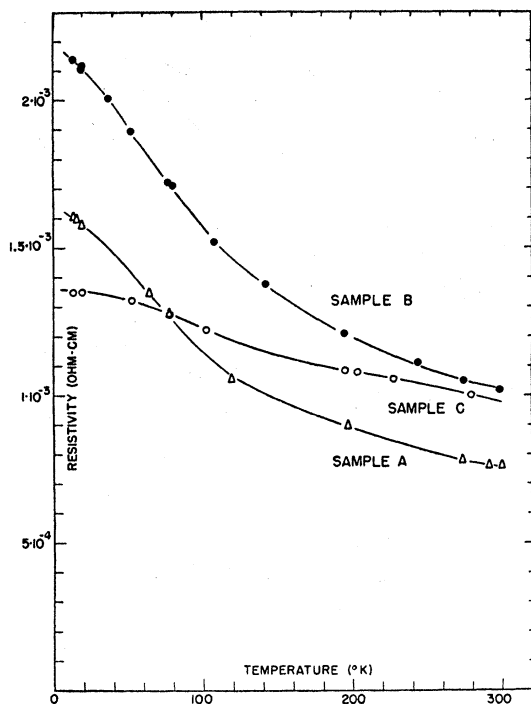


FIG. 3. Electrical resistivity as a function of temperature for samples A, B, and C.

in magnitude to that of A and B but less temperature dependent.

Figure 5 gives Wiedemann-Franz ratios computed from the curves of Figs. 2-4. This ratio is the same for samples A and B within several percent throughout the temperature range, and they are represented by the same curve. Figure 6 shows the absolute thermoelectric power for three samples, calculated from measured values of the thermoelectric power of graphite against constantan. The absolute thermoelectric power of constantan was obtained from the copper-constantan calibration, using data given by Borelius⁸ for the absolute thermoelectric power of copper. Thermoelectric power values for the graphite samples were also obtained from graphite-copper data and checked against the values given here. The thermoelectric power data are probably accurate to within 0.5 microvolt.

IV. DISCUSSION AND INTERPRETATION

(a) Thermal Conductivity

The Wiedemann-Franz ratio for extruded graphite at room temperature is about 200 times the free electron theoretical value (2.45×10^{-8} volt²/deg²) for a solid in which thermal conductivity is solely by electrons. At 90°K this ratio is about 520 times the theoretical value. As shown in Figure 5, the magnitude of the ratio depends on the temperature and on the type

⁸ G. Borelius, *Handbuch der Metallphysik* (Akad. verlags. Gesellschaft, Leipzig, 1935), Vol. I, pp. 181-520.

of graphite. At high temperatures⁹ and at low temperatures⁴ the ratio approaches the theoretical value. Because of the high value of the Wiedemann-Franz ratio and because of its dependence on temperature and type of graphite, it is concluded in agreement with Berman⁴ and Mrozowski¹⁰ that the thermal conductivity is due primarily to the transfer of energy by lattice vibrations.

The simple Debye expression for lattice conductivity^{11,12} indicates that

$$K = \frac{1}{3} c_v \lambda v_g, \quad (2)$$

where K is the thermal conductivity, c_v the specific heat, λ an average mean free path for scattering of lattice waves, and v_g an average group velocity for the waves. For pure, single, nonmetallic crystals, λ dominates in determining the temperature dependence of K except at very low temperatures.¹³ At temperatures above the Debye temperature, c_v is constant and λ is inversely proportional to the temperature. At temperatures below the Debye temperature, although c_v is decreasing, K increases exponentially with decreasing temperature due to the very rapid increase of λ . At sufficiently low temperatures λ becomes limited by the scattering of lattice waves from the boundaries of the crystal, and the conductivity reaches a maximum value. For lower temperatures, K decreases, being dominated by c_v .

The temperature dependence of conductivity indicates that boundary scattering in polycrystalline

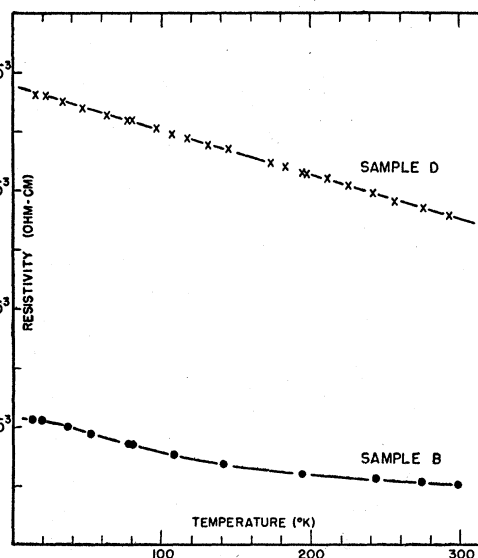


FIG. 4. Electrical resistivity as a function of temperature. Sample B is compared with the higher resistivity lampblack graphite, sample D.

⁹ R. W. Powell and F. H. Schofield, *Proc. Phys. Soc. (London)* **51**, 153 (1939).

¹⁰ S. Mrozowski, *Phys. Rev.* **86**, 251 (1952).

¹¹ P. Debye, *Vortrage über die Kinetische Theorie der Materie und der Elektrizität* (B. G. Teubner, Leipzig, 1914).

¹² R. Peierls, *Ann. Physik* **3**, 1055 (1929).

¹³ Berman, Simon, and Wilks, *Nature* **168**, 277 (1951).

graphite becomes important at relatively high temperatures. For samples A and B the maximum conductivity occurs at about 230°K. The maximum occurs near room temperature for sample C and above room temperature for sample D. Assuming that v_g is about 10^5 cm/sec, substitution of values of K and c_v ¹⁴ corresponding to the temperatures of maximum conductivity into Eq. (2), leads to the following approximate values of effective crystallite sizes, λ_{\max} .

Sample	λ_{\max}
A	6700A
B	5000A
C	1800A
D	< 500A

In bounding λ_{\max} for Sample D, we assume that c_v increases more rapidly than K from room temperature to the conductivity maximum.

The magnitudes of crystallite sizes deduced in this manner are not inconsistent with x-ray data, which, however, are not capable of distinguishing between the estimated sizes for samples A, B, and C. The difference in the effective crystallite sizes of samples A and B is presumably due to differences in orientation. Sample C is somewhat anomalous as there is no reason to believe that its crystallite size should be smaller than for samples A and B.

According to the interpretation based on Eq. (2), at temperatures considerably below the maximum the thermal conductivity should be proportional to the specific heat. This is not observed, the specific heat of artificial graphite being quite accurately proportional to T^2 in the temperature range from 20°K to 50°K,¹⁴ whereas the thermal conductivity in the same temperature range, for samples A, B, and C is proportional to T^n where n is estimated to be 2.7 ± 0.3 . The conductivity of sample D is more nearly proportional to T^2 , but the

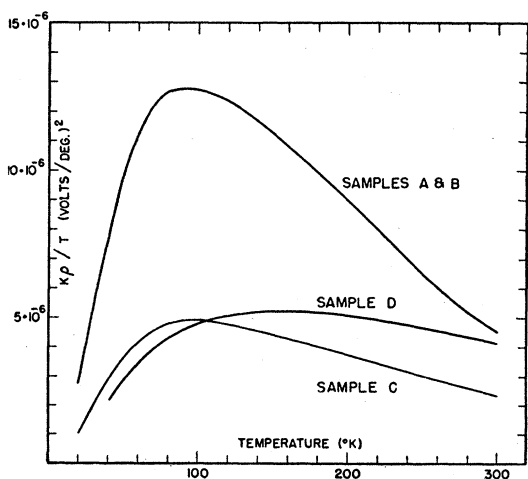


FIG. 5. Wiedemann-Franz ratio as a function of temperature. Values were calculated from the smoothed curves of Figs. 2, 3, and 4.

¹⁴ W. W. Tyler and W. DeSorbo, Phys. Rev. 83, 878 (1951).

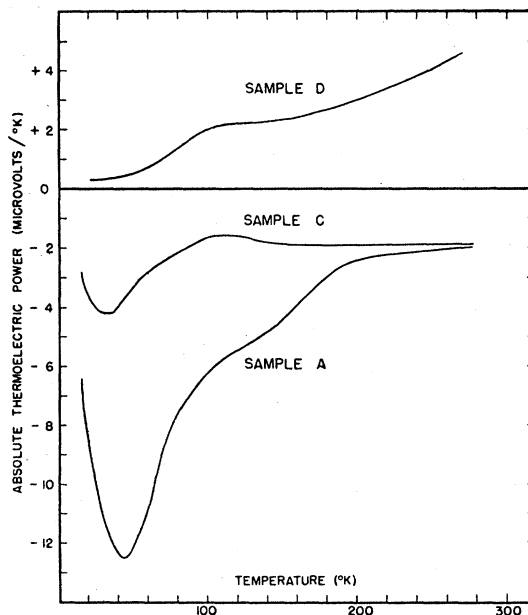


FIG. 6. Absolute thermoelectric power as a function of temperature. Values were obtained from measurements of thermoelectric power of constantan-graphite and copper-graphite couples.

uncertainty in the low conductivity values makes it difficult to assign much quantitative significance to its temperature dependence. The failure of the Debye relationship in explaining the temperature dependence of the conductivity may be related to the large anisotropy of the graphite structure. However, examination of the more detailed expression for the conductivity,¹⁵ which permits λ and v_g to depend on the wave vector, does not suggest an obvious explanation of the discrepancy. The explanation may be related to the temperature dependence of the energy transfer across crystallite boundaries. Densities of the graphites studied are about $\frac{3}{4}$ theoretical density for graphite, and it is easy to believe that the transport phenomena will be affected by temperature dependent interface properties.

(b) Electrical Resistivity

For a perfect single crystal of graphite, the two-dimensional Wallace theory¹⁶ predicts that

$$\rho = C/(\tau_T 2kT \log 2), \quad (3)$$

where ρ is the resistivity, C a collection of constants and τ_T the mean time for scattering of electrons from lattice vibrations. In order to satisfy the observed positive resistivity *vs* temperature slope for single crystals, Wallace assumes that the temperature dependence of τ_T is given by T^{-n} where n is greater than unity.

For polycrystalline graphite we assume that¹⁷

$$1/\tau = 1/\tau_T + 1/\tau_0,$$

¹⁵ P. G. Klemens, Proc. Roy. Soc. (London) A208, 108 (1951).

¹⁶ R. P. Wallace, Phys. Rev. 71, 622 (1947).

¹⁷ D. Bowen, Phys. Rev. 76, 1878 (1949).

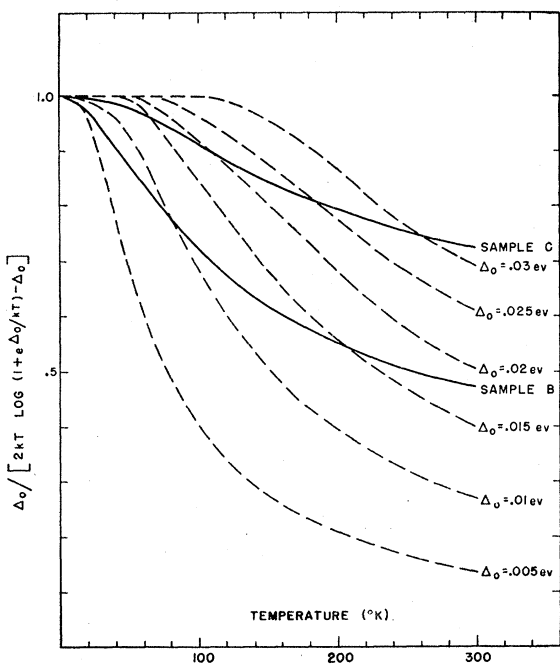


FIG. 7. Comparison of experimental resistivity data with the theoretical expression (6). Experimental and theoretical values are adjusted to a value of unity at absolute zero.

where τ_0 is the mean free time for scattering of electrons from imperfections and crystallite boundaries and is assumed to be independent of temperature. This gives

$$\rho = C' \left(\frac{1}{\tau_T} + \frac{1}{\tau_0} \right) \frac{1}{2kT \log 2}, \quad (4)$$

where C' now contains a geometric factor related to the density and preferred orientation of the crystallites. At sufficiently low temperatures τ_T becomes large compared with τ_0 , and

$$\rho = \frac{C'}{\tau_0} \frac{1}{2kT \log 2}. \quad (5)$$

This gives a resistivity vs temperature slope which is negative in agreement with experimental results for room temperature and below. However, (5) predicts a hyperbolic dependence of ρ on T which does not agree with experimental results at low temperature. Extrapolation of the curves of Figs. 3 and 4 suggests finite resistivity-temperature slopes at 0°K.

The above expressions are based on the assumption that the Fermi level remains at the Wallace zone boundary. If because of impurity or surface states, the Fermi level is displaced from the zone boundary by an amount Δ , it may be shown¹⁸ that

$$\rho = \frac{C'}{\tau_0 [2kT \log(1 + e^{\Delta/kT}) - \Delta]}, \quad (6)$$

¹⁸ Gerhart Hennig, J. Chem. Phys. **19**, 922 (1951).

where again we assume $\tau_T \gg \tau_0$. For $\Delta = 0$, expression (6) reduces to expression (5). For $\Delta \gg kT$, (6) reduces to

$$\rho = C'/\tau_0 \Delta. \quad (7)$$

In this case the temperature dependence of ρ is given by the temperature dependence of Δ . For any finite Δ , in the limiting case as $T \rightarrow 0$,

$$\rho_0 = C'/\tau_0 \Delta_0, \quad (8)$$

where Δ_0 is the deviation of the Fermi level from the zone boundary at absolute zero.

It is of interest to compare the experimental data with Eq. (6) under the assumption that Δ is independent of temperature. Figure 7 shows the function $\Delta_0 / [2kT \log(1 + e^{\Delta_0/kT}) - \Delta_0]$ plotted against temperature for different values of Δ_0 ranging from 0.005 eV to 0.03 eV. The solid curves give relative values of experimental data for samples B and C. Relative resistivity values for sample A are within 5 percent of those for sample B and are not plotted separately. As the experimental data extend down only to about 14°K, it was necessary to extrapolate to absolute zero, and comparison of the behavior of the theoretical and experimental curves in the neighborhood of zero temperature is not too meaningful.

The simplicity of Eq. (8) does permit a direct interpretation of the extrapolated intercept value of resistivity. However, assuming that a reasonable estimate could be given for C' , it is still only possible to deduce the value of the product $\tau_0 \Delta_0$ from the intercept value. The deviation of the Fermi level from the zone boundary is presumably due to the trapping of electrons at atomic imperfections or crystallite boundaries. As these also contribute to the scattering of electrons, τ_0 and Δ_0 are not independent, although it is not possible to predict their exact relationship except on the basis of rather simple models.

The agreement between the data and Eq. (6) may be improved by allowing the magnitude of Δ to increase with temperature. This is particularly true for sample D for which the resistivity is observed to be a simple function of temperature. Because of the small crystallite size in sample D, it is reasonable to assume that $\Delta \gg kT$ and that Eq. (7) is applicable. If so, the assumption that

$$\Delta = \alpha + \beta T,$$

where βT is small compared with α throughout the temperature range, yields Eq. (1) immediately from Eq. (7). Insertion of a similar temperature dependence of Δ in Eq. (6) gives a better representation of the data for all the samples. It should be noted that as expression (6) is symmetric in the sign of Δ , it is only the temperature dependence of the magnitude of Δ which is important to consider here.

Although a temperature dependence of Δ of the type assumed above gives a better representation of the data, it is not in agreement with the Wallace theory. Hennig¹⁸ has calculated the temperature dependence of

Δ based on the two-dimensional Wallace theory. Because of the nature of the distribution of energy states near the zone boundary, the theory predicts that the magnitude of Δ decreases with increasing temperature. Attempts to fit our data to Eq. (6), assuming that the magnitude of Δ decreases with increasing temperature, result in poorer agreement than that shown in Fig. 7.

In the above discussion, it has been assumed that $\tau \gg \tau_0$ and that τ_0 is independent of temperature. If scattering of electrons by lattice vibrations begins to contribute appreciably below room temperature, the inclusion of this effect in the theoretical expression (6) would give better agreement with the data. Permitting τ_0 to depend on temperature could also result in better agreement. In fact, it is certainly not clear that scattering effects owing to boundaries are temperature independent and that all other boundary effects on the electronic properties may be included in Δ . However, on the basis of the experimental information available, it does not seem fruitful to speculate further on possible temperature dependence of Δ and τ_0 or the possible importance of lattice scattering.

(c) Thermoelectric Power

At present, there is no theory of thermoelectric power in graphite, and we will make no attempt to interpret the temperature dependence of the data. It should be pointed out that the sign of the thermoelectric power in graphite does not necessarily coincide with the sign of the Hall coefficient. Measurements at room temperature indicate that the sign of the Hall coefficient for all four graphite samples studied is negative. Thus, sample D which has a positive thermoelectric power throughout the temperature range studied has a negative Hall coefficient at room temperature. Approximate values of Hall coefficients for the four samples are given below.

Sample	R (emu)
A	-0.66
B	-0.48
C	-0.59
D	-0.37

These values of Hall coefficient are in fair agreement with values quoted by Hennig¹⁸ and Donoghue and Eatherly¹⁹ for well-graphitized material. Studies of the

¹⁹ J. J. Donoghue and W. P. Eatherly, *Rev. Sci. Instr.* **22**, 513 (1951).

effect of oxidation¹⁸ or degree of graphitization¹⁹ on the Hall coefficient indicate that the sign of the Hall coefficient can be controlled to some extent and that presumably samples with Δ equal to zero could be prepared. The low temperature resistivity of such a sample should be given by Eq. (5). Observation of this would give some evidence for the correctness of the theory.

V. CONCLUSION

The results presented indicate the general magnitude and temperature dependence of the properties studied but do not permit entirely satisfactory theoretical interpretation. Refinement of the measurements and their extension to lower temperatures and to a larger variety of graphites may lead to a better understanding of the transport phenomena. However, it seems probable that satisfactory understanding will await measurements on single crystals. Lack of knowledge of the magnitude, temperature dependence, and anisotropy of thermal conductivity in pure single crystals seriously limits efforts to estimate the effects of orientation, crystallite size, and energy transfer across crystallite boundaries on the conductivity of polycrystalline material. Of particular fundamental interest is knowledge of the normal modes which predominate in determining the temperature dependence of the conductivity, the nature of interactions among these modes, and between these modes and free electrons. Interpretation of electrical resistivity and thermoelectric power measurements is also complicated by the polycrystalline nature of the graphites studied and will probably remain uncertain until single crystal experiments test the applicability of the Wallace theory and the effect of the controlled introduction of imperfections.

The work reported was done at the General Electric Company Low Temperature Laboratory and benefited from the cooperation of all members of the Laboratory. W. DeSorbo, M. D. Fiske, and R. W. Powers contributed helpful suggestions concerning experimental techniques. The interpretation of experimental results has been stimulated by discussion with J. P. Howe, J. A. Krumhansl, R. L. Cumberow, and J. B. Sampson of the Knolls Atomic Power Laboratory. Finally, we are indebted to W. C. Dunlap, Jr., and E. M. Pell for measuring Hall coefficients of our samples.