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THERMAL CONDUCTIVITY, ELECTRICAL RESISTIVITY
AND THERMOELECTRIC POWER OF GRAPHITE

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ABSTRACT

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, due to an excess or deficit of electrons. Scattering of electrons in the temperature range of interest is attributed to crystallite boundaries or impurities 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.

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I. Samples Studied

The four 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 gm/cm^3 . 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 gm/cm^3 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 gm/cm^3 . The axis of sample D is parallel to the preferred c_0 axis orientation although due to the small crystallite size orientation effects are small for this type of graphite.

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 Figure 1 is evacuated during measurements to about $5 \cdot 10^{-6} \text{ mm}$ 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 T and the average 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 ⁽¹⁾. The block heater and heat leak permit measurements in temperature regions between various bath temperatures. This technique ⁽²⁾ has been used extensively by Powers and is described by him 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 sensitivity of the system is about 0.03 microvolts. Use of either the copper or constantan elements of TC-5 and TC-6 as potential leads permit 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 either by the titanium hydride process ⁽³⁾ or by ordinary soft soldering 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" 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 due 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 may be made using data of Powers⁽²⁾ 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 $\pm 5\%$ for the highest conductivity points and $\pm 15\%$ for the lowest conductivity points.

Our conductivity data for samples A and B agree well with data of Berman⁽⁴⁾ and Rasor⁽⁵⁾ for samples of extruded graphite which are probably similar to our samples. Our data do not agree with data of Bierschaper⁽⁶⁾ which indicates that the conductivity of graphite continues to increase as the temperature decreases down to 90°K. It is felt that the method used by Bierschaper is less direct and more subject to error than our method.

Figure 3 shows the 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 $\pm 0.5\%$ except for a temperature independent, geometric error of at most 2% . The temperature dependence of the resistivity of samples A and B agree fairly well with work of Goetz and Holser⁽⁷⁾ 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 $7.75 \cdot 10^{-3}$ ohm-cm and B is $7.43 \cdot 10^{-6}$ ohm-cm/deg. Sample C has a resistivity comparable in magnitude to that of A and B but less temperature dependent.

Figure 5 gives the Wiedemann-Franz ratio computed from the curves of Figures 2, 3, and 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 Porelius⁽⁸⁾ 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 microvolts.

IV. Discussion and Interpretation

a. Thermal Conductivity

The Wiedemann-Franz ratio for extruded graphite at room temperature is about 200 times the theoretical value ($2.45 \cdot 10^{-8}$ volts²/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 of graphite. At high temperatures⁽⁹⁾ and at low temperatures⁽⁴⁾ 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 Berman⁽⁴⁾ and Mrozowski⁽¹⁰⁾ 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, non-metallic 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 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 corresponding to the temperatures of maximum conductivity into equation (1), leads to the following values of effective crystallite sizes, $\lambda_{\max}$.

<u>Sample</u>	<u>$\lambda_{\max}$</u>
A	5100Å°
B	3700Å°
C	1400Å°
D	< 400Å°

In bounding $\lambda_{\max}$ for sample D, we assume that c_v varies 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 equation (1), 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 $2.7 \pm .3$. The conductivity of sample C is more nearly proportional to T^2 but the 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. (15) However, examination of the more detailed expression for the conductivity, 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 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

We will interpret the resistivity data in terms of extensions of the (16) Wallace zone theory of graphite. For a perfect single crystal, the two-dimensional theory predicts that

$$\rho = \frac{C}{\tau_f 2kT \log 2} \quad (3)$$

where ρ is the resistivity, C a collection of constants and τ_f 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 ρ is given by T^{-n} where n is greater than unity.

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(17)
For polycrystalline graphite we assume that

$$\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_0}$$

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

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

where C' now contains a geometric factor related to the density and orientation of polycrystals. At sufficiently low temperatures τ_r 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 our experimental results at low temperature. Extrapolation of the curves of Figures 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 due to impurity or surface states, the Fermi level is displaced from the zone boundary by an amount Δ , it may be shown (18) that

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

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

$$\rho = \frac{C'}{\tau_0 \Delta} \quad (7)$$

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 $T \rightarrow 0$

$$\rho_0 = \frac{C'}{\tau_0 \Delta_0} \quad (8)$$

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

The general expression (6) predicts that for a finite Δ , the resistivity curves extrapolate into the zero temperature axis with a finite slope and thus permits interpretation of the intercept value. Unfortunately, only the product $\tau_0 \Delta_0$ may be deduced from the intercept value, assuming a reasonable theoretical estimate could be given for C' . As the deviation of the Fermi level from the zone boundary is related to the trapping of electrons or holes at imperfections or crystallite surfaces, τ_0 and Δ are not independent although it is not possible to predict their exact relationship except on the basis of rather simple models.

Temperature dependence of Δ for the two dimensional Wallace theory has been calculated by Hennig⁽¹⁸⁾. Due to the nature of the distribution of energy states near the zone boundary, the theory predicts that the magnitude of Δ decreases with increasing temperature. This is not in agreement with our results and thus casts some uncertainty on the interpretation of our results in terms of equation (6). The difficulty is most easily seen in studying the results for sample D. We have seen that the resistivity may be represented by

$$\rho = A - BT$$

Such a dependence is predicted directly by equation (7) with

$$\Delta = \alpha + \beta T \quad (9)$$

where we assume that $\Delta \gg kT$ in the temperature range of interest. Resistivity curves for the other samples may be represented quite well by equation (6) but again the best fit is always obtained when the magnitude of Δ is allowed to increase with increasing temperature.

Although the interpretation based on equation (6) is not completely satisfactory, there seems to be no necessity for accepting Krozowski's (19) assumption of the existence of a finite band gap in polycrystalline graphite. Even with the assumption of a temperature independent Δ , equation (6) permits a more accurate description of the low temperature data than does Krozowski's empirical equation (1). However, as pointed out above, the graphites studied are quite porous and the crystallites are bonded together in a manner which is not understood. It is not clear that scattering effects due to the boundaries are temperature independent and that all other boundary effects on the electronic properties may be included in Δ .

c. Thermoelectric Power

Expression (6) for the resistivity is symmetrical in the sign of Δ . Observation of a negative Hall coefficient for artificial graphite and the negative thermoelectric power of samples A and C indicates that these materials are characterized by an excess of electrons and that the Fermi level is above the zone boundary. However, the lampblack graphite has a positive thermoelectric power indicating that the Fermi level is below the zone boundary and that the conduction is mostly by holes. Studies of Hall coefficient (18, 20, 21) and thermoelectric power (22) in carbons and graphite indicate that Δ is a complicated function of degree of graphitization, impurities, and presumably, crystallite size. Hennig (18) has shown in detail that the sign of the Hall coefficient changes on oxidation of graphite and correlated these measurements with resistivity measurements. The possibility of controlling Δ suggests that graphite samples with Δ equal to zero could be prepared. The low temperature resistivity of such a sample should be given by expression (5) and observation

of this would be an interesting confirmation of the ideas used in interpretation of resistivity data.

IV. Conclusion

The results presented indicate the general magnitude and temperature dependence of the properties studied but do not permit 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 measurements is also complicated by the polycrystalline nature of the graphites studied. The resistivity and thermoelectric power measurements suggest that crystallite boundaries and impurities not only scatter electrons but have a pronounced effect on the position of the Fermi level, presumably by trapping electrons. The two effects are related in a manner which depends on the exact nature of the scattering center. Interpretation of electronic transport data in polycrystalline graphite will probably remain uncertain until single crystal experiments test the applicability of the Wallace theory and the effect of the controlled introduction of imperfections.

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LIST OF REFERENCES

1. T. Rubin, H. L. Johnston and H. Altman, Jour. Am. Chem. Soc., 73, 3401 (1951). We are indebted to W. DeSorbo for providing us with the thermocouple wire and calibration charts.
2. R. W. Powers, papers in process of publication.
3. R. J. Bondley, Electronics 20, 97 (1947).
4. R. Berman, Phys. Rev., 76, 315 (1949);
Private communication, August, 1951;
Paper in process of publication.
5. N. S. Rasor, Unpublished data. We are indebted to J. P. Eatherly for informing us of this recent work at North American Aviation Co.
6. R. A. Buerschaper, Jour. Appl. Phys., 15, 452 (1944).
7. A. Goetz and A. Holser, Trans. Electrochem. Soc., 82, 391 (1942).
8. G. Borelius, "Physikalische Eigenschaften der Metalle," Handbuck d. Metallphysik, I, pp 181-520, Leipsig, 1935.
9. R. W. Powell and F. H. Schofield, Proc. Phys. Soc., 51, 153 (1939).
10. S. Mrozowski, Phys. Rev., 86, 251 (1952).
11. P. Debye, "Vortraege ueber die kinetische Theorie der Materie und der Elektrizitaet," Teubner, 1914.
12. R. Peierls, Ann. d. Physik 3, 1055 (1929).
13. R. Berman, F. E. Simon and J. Wilks, Nature 168, 277 (1951).
14. W. W. Tyler and W. DeSorbo, Phys. Rev. 83, 878 (1951).
15. P. G. Klemens, Proc. Roy. Soc. A, 208, 108 (1951).
16. R. P. Wallace, Phys. Rev. 71, 622 (1947).
17. D. Bowen, Phys. Rev. 76, 1878 (1949).
18. Gerhart Hennig, Jour. Chem. Phys. 19, 922 (1951).
19. S. Mrozowski, Phys. Rev. 85, 609 (1952).
20. J. P. Eatherly and J. J. Donoghue, RSI, 22, 513 (1951).
21. K. Onnes and K. Hoff, Comm. Phys. Lab. University Leiden XIII, #142 (1914).
22. E. E. Loebner, Phys. Rev. 84, 153 (1951).

FIGURE 1

FIGURE 3

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FIGURE 4

FIGURE 5

FIGURE 6