PHYSICAL REVIEW VOLUME 104, NUMBER 4 NOVEMBER 15, 1956

Interpretation of the Low-Temperature Thermal Conductivity of Graphite*

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(Received March 23, 1956)

The experimental data observed by Smith and Rasor in measuring the low-temperature thermal conductivity of several types of graphites are interpreted on the basis of a two-medium theory. The theory assumes that, in the artificial polycrystalline graphites, the nongraphitic regions are isotropic thermal conductors and that these regions can be taken in series with the graphite particles to obtain a total conductivity. In this way, the anomalous temperature dependence of the artificial graphites can be immediately explained. Using this theory as a guide, the crystallite size of a given sample can be found in an unambiguous manner, and for the various graphite types discussed by Smith and Rasor are found to correlate with independent previous estimates. Furthermore, the observed effects of neutron damage and bromination can be readily explained in a phenomenological manner. Although this theory still needs refining in several aspects, it appears to be substantiated by all the available evidence and helps to establish the usefulness of low-temperature thermal conductivity measurements as a probe to detect internal defects and microstructure ln graphite.

I. INTRODUCTION

IN the previous paper[1] (hereafter referred to as I), experimental data on the low-temperature thermal conductivity of various graphites have been presented. In the present paper, a brief theoretical background of lattice thermal conductivity will be presented and a theory developed to interpret the observed results for graphite, which appear to show an anomalous temperature dependence at low temperatures (see the preceding paper). This interpretation is based on the fact that artificial, polycrystalline graphite is made up of two media, the graphite particles and ungraphitized pitch residue. As a model, to make the present discussion somewhat easier, the ungraphitized region will be considered as the bonding material between the graphite particles. However, it should be pointed out[2] that in many graphites an appreciable amount of the pitch itself becomes graphitized, which may make the above model somewhat inaccurate. This is not a crucial matter, as far as the present work is concerned, since those graphitized parts of the pitch residue can just as well be considered as new graphite particles, although with more indistinct boundaries. Furthermore, the most interesting results obtained below require only that such ungraphitized material exist in sufficient quantity to form three-dimensionally isotropic heat conductors in series with the graphitic region. Thus, the precise model used is not of great importance. For this same reason, we shall neglect the explicit effects of void spacing, which will exist predominantly in the nongraphitic regions. It is clear, of course, that a more refined theory than that developed herein must take the above items into consideration; thus, it then becomes a task of great magnitude.

On the basis of quantitative analyses, considering the effects of neutron damage and bromination as well as graphite type and temperature, the two-medium hypothesis appears to explain the behavior of the thermal conductivity of artificial graphites in a satisfactory manner. An alternate interpretation, which the authors consider less satisfactory, will be discussed also. It should perhaps be emphasized that the present work is largely phenomenological and little effort has been made in this paper to derive the fundamental phonon scattering processes.

II. THEORY OF THERMAL CONDUCTIVITY IN GRAPHITE

It has been shown[3] that the conduction of heat in graphite takes place mainly by lattice waves rather than by electronic transport. The principal evidence for this is the experimental value of the Wiedemann-Franz ratio which, at least for room temperature and below, is 10 to 100 times larger than the theoretical value. This is observed in both single crystal[4] and polycrystalline form.

Several authors[5,6] have considered the theory of heat conduction in crystalline lattice conductors. If the dissipation of energy out of a given normal mode can be described by a relaxation time, τ_j, it is a simple matter to show that the thermal conductivity tensor is

$$\kappa_{mn}=\sum_j c_j\tau_j(\mathbf{v}_j)_m(\mathbf{v}_j)_n, \tag{1}$$

where c_j is the specific heat associated with the mode j and $\mathbf{v}_j$ is the group velocity of that mode.

If we define $\mathbf{q}$ as the wave vector, Eq. (1) can be

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[1] A. W. Smith and N. S. Rasor, Phys. Rev. **103**, 885 (1956), preceding paper.

[2] The authors are indebted to H. S. Pattin and others of the National Carbon Research Laboratories for discussions of this point.

[3] W. W. Tyler and A. C. Wilson, Jr., Phys. Rev. **89**, 870 (1953).

[4] A. W. Smith, Phys. Rev. **95**, 1095 (1954); also, see preceding paper, reference 1.

[5] P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951), and references therein.

[6] C. Herring, Phys. Rev. **95**, 954 (1954).

written

$$\kappa_{mn}=\sum_i \int c(\omega_i)d\omega_i(2\pi)^{-3}\int\int dS \times|\nabla_q\omega_i|^{-1}\tau_i(\partial\omega_i/\partial q_n)(\partial\omega_i/\partial q_m), \quad (2)$$

where ω is the frequency and i refers to the polarization branch of the acoustical modes, thus taking on three values. The optical modes are generally of no consequence here because of their low group velocity. The surface integral extends over a surface of constant frequency in q space and the frequency integration is over all allowed values. If τ_i is a function of ω_i only, the nondiagonal terms will vanish; this will be assumed throughout the present paper.

If the constant frequency surfaces are spherical, the group velocity has no angular dependence and $(\partial\omega/\partial q_m)^2$ may be replaced by its average value of $\frac{1}{3}|\nabla_q\omega|^2$. Equation (2) then reduces to

$$\kappa_{mm}=\tfrac{1}{3}\sum_i \int c(\omega_i)l(\omega_i)v(\omega_i)n(\omega_i)d\omega_i, \quad (3)$$

where $v(\omega)$ is the magnitude of the group velocity, $l(\omega)$ is the mean-free path defined as $v(\omega)\tau(\omega)$, and $n(\omega)$ is the density of modes. This is the form obtained by Klemens[5] for an isotropic solid, although his derivation is some what longer.

Graphite is so anisotropic that it is very nearly valid to consider its constant ω surfaces as cylindrical with a zero group velocity along the z axis.[7] Under these conditions, $(\partial\omega/\partial_{qm})^2$ can be replaced by its two-dimensional average value of $\frac{1}{2}|\nabla_q\omega|^2$, where m takes on two values only. This leads to

$$\kappa_{mm}=\tfrac{1}{2}\sum_i \int c(\omega_i)l(\omega_i)v(\omega_i)n(\omega_i)d\omega_i; \quad (4)$$

that is, the same analytical expression as Eq. (3) except for the numerical coefficient. It might be noted that despite this, the factor of $\frac{1}{3}$ has been used rather consistently in the literature on thermal conductivity of graphite. If the group velocity and mean-free path are assumed independent of frequency, Eq. (4) becomes

$$\kappa=\tfrac{1}{2}\sum_i C_i l_i v_i, \quad (5)$$

where C_i is the total specific heat per unit volume of the branch i. This expression should be valid at low temperatures where the scattering is due to crystallite boundaries and the group velocity is a constant, if one assumes Debye-like dispersion. In this case, one could reasonably assume that all the acoustic modes have the same scattering path. If all three modes are Debye-like, one is led to conclude that the temperature dependence of the thermal conductivity, at low temperatures, should be the same as that of the specific heat. If the temperature is not low enough to cause the scattering to be frequency-independent, the temperature dependence of the thermal conductivity should be weaker than that of the specific heat, under the above assumptions.

The observed fact, in graphite, is that the temperature dependence of the thermal conductivity at low temperatures (10° to 50°K) varies from T^2 to T^3 (depending on the type of graphite) whereas the specific heat,[8] in this same temperature region, varies as T^2. This constitutes the anomaly mentioned in the previous paper (I). It is conceivable that this might occur because polarization modes which are negligible for the specific heat become relatively enhanced by the scattering path or group velocity when thermal conduction is considered; this viewpoint must then assume that the enhanced modes introduce a new temperature dependence. An explanation of the anomaly has been advanced[9] based on this possibility, although for reasons to be discussed later, the authors believe that this interpretation is incorrect.

The explanation for this anomaly, offered in the present report, is taken to lie in the artificial nature of the graphites exhibiting the effect. The artificial graphites are made by bonding particles of coke or lampblack with pitch and heating to 2500°C or higher. Most of the carbon forms polycrystals of graphite, but some of the pitch does not graphitize. The model which we will assume considers the graphitic particles (each of which will be made up of many single crystallites) to be surrounded and bonded together by a nongraphic carbon region. In the absence of more definite information, it is reasonable to assume that this nongraphitic carbon has mostly tetravalent bonding and resembles a poorly crystallized, or highly disorganized, diamond-like structure. Therefore, at low temperatures, this region will be assumed to conduct heat in a three-dimensionally isotropic manner with a Debye-like dispersion. The Debye temperature will be taken as 3000°K, i.e., about the same as diamond, although the actual value assumed does not critically affect the analysis.

It can now readily be seen how this explanation qualitatively predicts the temperature dependence of the thermal conductivity at low temperatures. The thermal resistivity of the graphitic regions is inversely proportional to the specific heat of graphite and is therefore proportional to T^{-2}, where T is the absolute temperature, at low temperatures. In an analogous manner, it is seen that the thermal resistivity of the nongraphitic regions is proportional to T^{-3}, since the specific heat, at low temperatures, of an isotropic, Debye-like solid is proportional to T^3. If these two regions are in series, the total thermal resistivity is approximately equal to their sum and therefore will behave as T^{-3} at very low temperatures and T^{-2} at

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[7] J. Krumhansl and H. Brooks, J. Chem. Phys. **21**, 1663 (1953).

[8] W. DeSorbo and W. W. Tyler, J. Chem. Phys. **21**, 1660 (1953).

[9] P. G. Klemens, Australian J. Phys. **6**, 405 (1953).

higher temperatures. This corresponds in a qualitative manner to the observed behavior (and especially correlates with the fact that the thermal resistivity of both natural single crystal and pyrolytized polycrystal graphites behave strictly as T^{-2}) and it now remains to formulate this hypothesis in a more precise manner to see if a quantitative analysis will yield the correct order of magnitude.

The total thermal resistivity can be written

$$\frac{1}{\kappa}=\frac{\alpha}{S\kappa_2}+\frac{(1-\alpha)}{\kappa_3}, \tag{6}$$

where κ_2 and κ_3 refer to the conductivities of the graphitic regions (essentially two-dimensional conduction) and the nongraphitic regions (three-dimensional) as explained above. The parameter α is the volume fraction of the specimen which is graphite and S is the effective fraction of the graphite which is oriented to permit a heat flow in the direction of the temperature gradient. The value of α can be independently estimated from measurements of the specific magnetic susceptibility and varies from 90 to 95% for the types of artificial graphite used in the previous paper (I). The value of S can be determined by the anisotropy ratio of electric conductivity and varies between 0.5 and 0.7 in the present case.

In the nongraphitic region, the phonon scattering mean-free path can be taken as a constant at low temperatures, corresponding to boundary scattering, and will be about the same for all three polarizations. Considering an averaged group velocity to be

$$v_3=(k\theta_3/h)(4\pi V_3/3N_3)^{\frac{1}{3}},$$

(where θ_3 is the corresponding Debye temperature and N/V is the atom density), the thermal conductivity can be written

$$\kappa_3=\tfrac{1}{3}C_3v_3l_3.$$

Here the specific heat per unit volume, C_3, is readily found to be (at low temperatures compared with θ_3)

$$C_3=240k(N_3/V_3)(T/\theta_3)^3,$$

and l_3 is the constant scattering path of the phonons.

In the graphitic region, only one polarization has been taken to be important, the transverse out-of-plane mode. The reason for this originally arose from the calculations of Krumhansl and Brooks,[7] who showed that, with a Debye temperature somewhat less than 1000°K, this mode could account for almost all the observed specific heat.[8] With this assumption, the conductivity of the graphite is

$$\kappa_2=\tfrac{1}{2}C_2v_2l_2,$$

where

$$v_2=(k\theta_2/h)(\pi A_2/N_2)^{\frac{1}{2}},$$
$$C_2=15k(N_2/V_2)(T/\theta_2)^2.$$

Note that the area density N/A arises in the group velocity because of its two-dimensional character (this is not the case for the specific heat since it is still defined as being per unit volume). The value of l_2 will be the crystallite length at the lowest temperatures, provided the temperature is not so low as to make interplane interactions important; this critical temperature is probably less than 10°K. It should be pointed out that later calculations of the specific heat of graphite[10] indicate the possibility that, while the out-of-plane mode is largely responsible for the specific heat, the softer of the two in-plane modes is the major contributor to the thermal conductivity. This in-plane mode has a theoretical Debye temperature of about 1600°K. It may be noted, however, that the graphite thermal resistivity depends on the first power of θ_2 only, so that such a change in the Debye temperature (that is, 1600°K instead of 1000°K) will affect the specific heat much more than the conductivity. Therefore, this new possibility as to the responsible mode will not affect the order of magnitude of our present results, which, by the nature of the assumptions used, cannot be considered as being very precise.

In computing the velocities and specific heats, a diamond structure was used for the three-dimensional region, although a graphitic interatomic distance (1.4 A) was assumed. By letting $\theta_2=1000$°K and $\theta_3=3000$°K and substituting all the values into the expression for the total thermal resistivity [Eq. (6)], the latter becomes

$$\frac{T^3}{\kappa}=\frac{\alpha T}{Sl_2}+\frac{60(1-\alpha)}{l_3}, \tag{7}$$

where both sides have, in addition, been multiplied by T^3. The units used are such that if the lengths are in centimeters, the thermal conductivity is in (cal/sec-cm-°K). The actual numerical coefficients in Eq. (7) have been rounded off to the values shown, in view of the approximations used. The value of α, the volume fraction of the sample which is graphitic, can be independently estimated from magnetic susceptibility measurements. The method is very straightforward and depends on the fact that carbon in graphitic form shows a much higher susceptibility than in nongraphitic form. Since the susceptibility of a single crystal is known,[11] an examination of the susceptibility value of a given graphite immediately yields the fraction which is graphitic. Similarly, the value of S, the effective fraction of the graphitic region which is favorably oriented, can be estimated for a given type of graphite, from the observed anisotropy of the electrical conductivity. Table I lists the values of these two parame-

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[10] W. P. Eatherly and J. A. Krumhansl (to be published); also, see G. F. Newell, Brown University Office of Naval Research Technical Reports, December 15, 1954 and May 15, 1955 (unpublished).

[11] W. Ganguli and K. S. Krishman, Proc. Roy. Soc. (London) **177**, 168 (1941).

TABLE I. Graphitization and orientation parameters.

Graphite type	α	S
AGOT-KC	0.91	0.7
AWG	0.91	0.4
SA-25	0.94	0.5
Pyrolytized	1.0	0.7
Canadian natural	1.0	1.0

ters for the various types of graphite reported in the preceding paper (I).

Note, now, from Eq. (7), that if the present formulation is correct, a plot of the experimental values of $T^3\kappa^{-1}$ against temperature should yield a straight line at the lowest temperatures. Since the parameters α and S can be considered known, the slope of this line is a direct measure of the graphitic crystallite size, while its intercept gives the scattering length in the nongraphitic region. The latter is related to the average distance between regions which are graphitized, and for order of magnitude purposes, can be considered equal to this distance. If the Debye temperatures assumed above are of the correct relative order of magnitude, the predominant wavelength, at a given temperature, in the ungraphitized regions will be greater by a factor of two or three than the predominant wavelength in the graphitic regions. For this reason, the waves in the graphite will begin to be scattered by internal defects of a given size at a lower temperature than the waves in the isotropic part. In addition, the crystallite size can be expected to be larger than the nongraphitic thickness and thus boundary scattering will predominate to a higher temperature in the latter case, further masking the effects of internal defect scattering in the nongraphitic region. The reasonable assumption will then be made that the temperature dependence of l_2 [in Eq. (7)] must be considered but that to a first approximation the value of l_3 can be taken as temperature-independent (i.e., as a boundary scattering path only).

The frequency dependence of the scattering path in the graphitic regions can only be qualitatively discussed in the present paper, since this clearly depends on the size and shape of the defect. If the size is much larger than the thermal wavelength, we get boundary, or frequency-independent, scattering; if the size is much smaller than the wavelength, Rayleigh scattering should result (if this were a line defect of small diametric size, one might expect Rayleigh scattering, but in one less dimension than the original medium). The internal defects of interest for the present discussion will be those which are large (but not large enough to constitute boundaries), since these are presumably the ones which first become important as the temperature is raised. Scattering from such defects is quite complicated but, for a phenomenological discussion, we shall assume that the scattering probability can be adequately described at low frequencies (i.e., long wavelengths) by the linear expression

$$1/l_2 = 1/L + aN\nu,$$

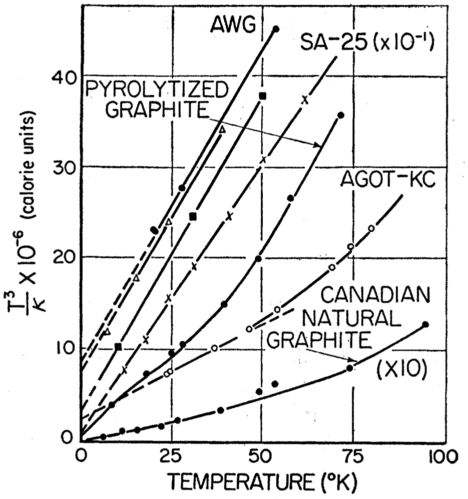

FIG. 1. Temperature dependence of the function $T^3\kappa^{-1}$ for several types of graphite. Note scale change for SA-25 and Canadian graphite data.

where L is the average crystallite length, ν is the frequency of the scattered wave, and N is the density of defects. This has the right qualitative behavior and cannot be very far from the correct expression, regardless of the type of scattering. Equation (7) then becomes

$$\frac{T^3}{\kappa} \simeq \left(\frac{\alpha}{SL}\right)T + \left(\frac{\alpha}{S}Ng\right)T^2 + \frac{60(1-\alpha)}{l_3}, \tag{8}$$

where g is a parameter including the new value of the Debye integral as well as the unknown constant a.

III. CORRELATION OF THEORY WITH EXPERIMENT

The final equation of the previous section represents the predicted low-temperature variation of the thermal conductivity of graphite. This has been obtained, as a first approximation, on the basis of a two-medium model of artificial graphite and contains three disposable parameters, the crystallite size (L), the average spacing between graphitic regions (l_3), and a number proportional to the density of internal defects (Ng). We now wish to compare this expression with the experimental data presented in the previous paper (I) both as to the form of the variation and as to the order of magnitude of these parameters.

A. Effect of Graphite Type

In Fig. 1 we replot the experimental data for types AGOT-KC, AWG, and SA-25 artificial graphites, along with the Canadian natural and the pyrolytized graphites, as $T^3\kappa^{-1}$ vs temperature. It can be seen that the data fit the form of Eq. (8) remarkably well, especially conconsidering the inherent difficulties of measuring the

TABLE II. Crystallite sizes as obtained from thermal conductivity.

Graphite type	Particle size	Estimated crystallite size	Value of L	Value of l_3
AGOT–KC	50 μ	≥ 3000 A	6200 A	2600 A
AWG(I)	25 μ	≥ 2000 A	3400 A	600 A
AWG(II)			3200 A	1600 A
SA-25	0.3μ	$\sim$500 A	300 A	280 A
Pyrolytized			3800 A	
Canadian		$\sim 10^{-2}$ cm	1.4×10^{-3} cm	

thermal conductivity at those low temperatures. Three independent curves for AWG are shown to illustrate the reproducibility of the linear slope, which is a measure of the crystallite size. The intercept varies somewhat from sample to sample and this is to be expected, since the average thickness of the nongraphitic region will depend strongly on such items as porosity, which can vary considerably for different specimens. It has been noted[12] that the observed specific heat of graphite varies more strongly than T^2 at temperatures around that of liquid helium. If this is a lattice effect, the thermal conductivity of the graphitic crystallites should show a similar behavior. While some data have been obtained at temperatures below 10°K which appear to show such a trend, we do not believe that these results are sufficiently precise to warrant any serious discussion at this time.

By substituting the linear slopes and intercepts from Fig. 1, and the parameter values from Table I, into Eq. (8), values for the crystallite size L and nongraphitic thickness, l_3, have been obtained. These values are shown in Table II along with independent estimates of the particle and crystallite sizes for these graphites. The crystallite sizes are seen to vary in the correct relative way from sample to sample and furthermore are of the same order of magnitude as the independent estimates. As a rough check on the nongraphitic thicknesses, l_3, obtained, the nongraphitic material may be assumed to be spread uniformly around the particle. The thickness of this layer should then be of the same order of magnitude as $(l_3)/2$. Taking spherical particles of diameter 3000 A for the SA-25 graphite, 6% of ungraphitized carbon (from Table I) thus leads to an "l_3" of 60 A. For the AGOT graphite, it is probably better to use a cylindrical slab for the particle shape, with a ratio of diameter to length of around 5. Taking the diameter to be 50 microns (Table II) and 9% of ungraphitized carbon (Table I), an "l_3" of 1000 A is then found. While this model is not to be taken too seriously, these figures indicate that the values of l_3 in Table II are reasonable.

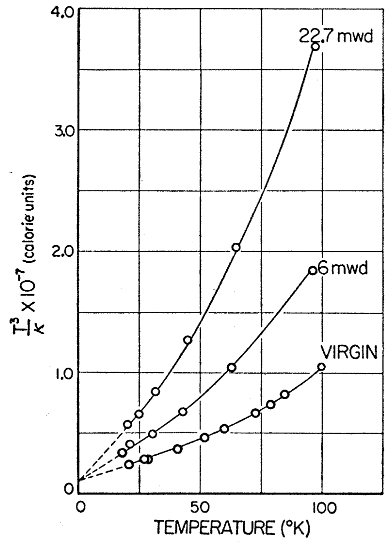

FIG. 2. Effect of neutron bombardment on the function $T^3\kappa^{-1}$ *vs* temperature for type AWG graphite. All irradiations were made at about 30°C. The unit Mwd (megawatt-day) corresponds approximately to a flux of 10^{17} *nvt* of neutrons with energy above 0.5 Mev.

B. Effect of Neutron Irradiation

The previous paper (I) shows the observed effect of neutron bombardment on the thermal conductivity. This effect is large and changes the temperature variation as well as the magnitude. The mechanisms of radiation damage in graphite have been discussed elsewhere[13] and it will suffice to mention here that the major effect of particle radiation is to introduce internal defects into the graphite specimen. To a lesser extent, the effective number of crystallite boundaries will be increased, but this is probably due to trapping of defects at small angle boundaries which were previously ineffective in scattering thermal waves. The internal defects will also trap electrons, thus changing the effective free electron concentration and causing striking changes in the electrical and magnetic properties of graphite.[14] The possibility that a major part of the change in thermal conductivity upon irradiation might be due to increased scattering of the phonons by the phonons by the new electron distribution was considered in some detail by the authors. It is not at all unreasonable that this could be the case since, as electrons are trapped, the Fermi level recedes from the edge of the filled band and graphite should then begin to look more like a good metal (in which phonon scattering by the electrons is known to be important). The experimental program to investigate this effect utilized the bromine-graphite residue compounds, which provide a method of trapping electrons without introducing large changes in internal defect scattering. This program is discussed in the previous paper (I) and yielded essentially the

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[12] Bergenlid, Hill, Webb, and Wilks, Phil. Mag. **45**, 851 (1954); also, see P. H. Keesom and N. Pearlman, Phys. Rev. **99**, 1119 (1955).

[13] G. R. Hennig and J. E. Hove, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1955* (Columbia University Press, New York, 1956), Vol. 7, Sec. 138, p. 666.

[14] W. P. Eatherly, Phys. Rev. **98**, 1531(T) (1955); also, see reference 13.

negative result that electron scattering gave much too small an effect (if, indeed, any effect at all) to account for the damage results. A concurrent theoretical analysis was also made of phonon-electron scattering,[15] which yielded the qualitative result that the observed change in the temperature dependence on irradiation was opposite to that theoretically predicted by assuming the electron scattering to predominate. From these studies it may be concluded that thermal conductivity in graphite has a negligible dependence on the electron concentration and thus is a valuable aid in attempting to discover the actual lattice changes which accompany neutron bombardment.

If the reasonable assumption is made that damage effects do not materially alter the structure of the already disordered nongraphite region, it is seen that neutron bombardment will mainly change the mean-free path in the graphitic crystallities. Referring to Eq. (8), this means that the major effect will be to increase the number of internal defects, N, in the coefficient of the second term, although the coefficient of the first term will also increase due to a decrease in the effective crystallite size, L. Figures 2, 3, and 4 show the neutron-irradiation data of Paper I replotted in the form $T^3\kappa^{-1}$ *vs* T. It is to be noted that the intercept of the curves does not change to any appreciable extent, thus verifying the assumption made above that the nongraphitic mean path, l_3, is not affected by bombardment. The slopes of the linear part of the curves apparently increase somewhat, as predicted, although the data are rather sparse in this temperature region.

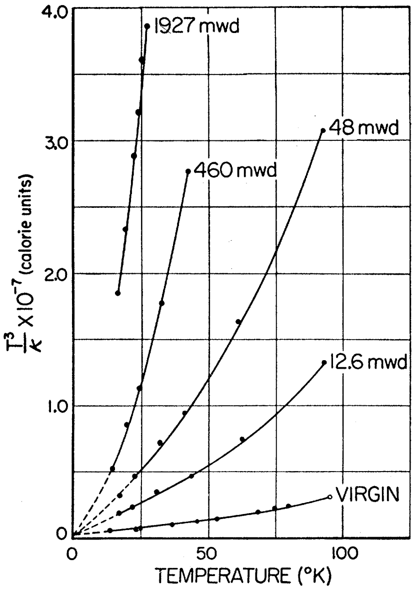

Fig. 3. Effect of neutron bombardment for type AGOT–KC graphite. Irradiations were made at about 30°C.

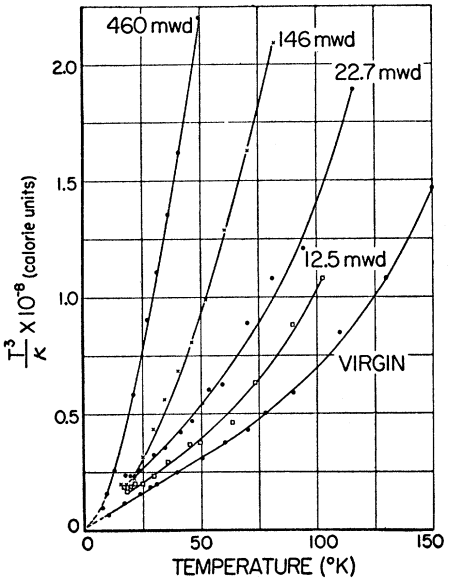

Fig. 4. Effect of neutron bombardment for type SA-25 graphite. Irradiations were made at about 30°C.

Figures 5, 6, and 7 show the above data plotted against T^2, so that the slope of the linear range is now proportional to the number of defects, N, according to Eq. (8). As expected, these slopes increase rapidly with increasing neutron exposure. By subtracting the initial (undamaged) slope, and correcting for the types of graphite, a function proportional to the number of neutron-induced internal defects ($N-N_0$), is obtained and is shown on Fig. 8. At present, we can offer no strong explanation for the effect of crystallite size shown on Fig. 8. As seen, the SA-25 graphite (with crystallites of the order of ten smaller than the other two graphites) appears to retain about twice as many defects as the others for a given neutron exposure. This may be apparent only, since the orientation and graphitization

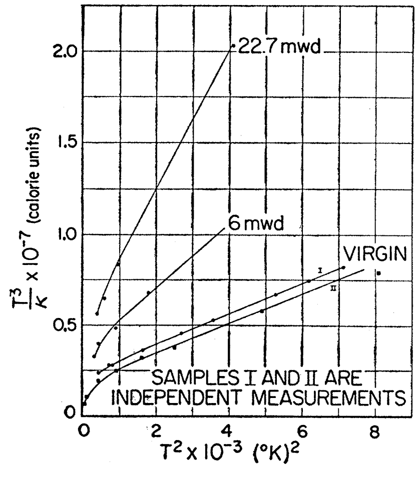

Fig. 5. The function $T^3\kappa^{-1}$ *vs* T^2 for AWG graphite with various neutron exposures.

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[15] J. E. Hove, North American Aviation Report NAA–SR–1398, January 1, 1956 (unpublished).

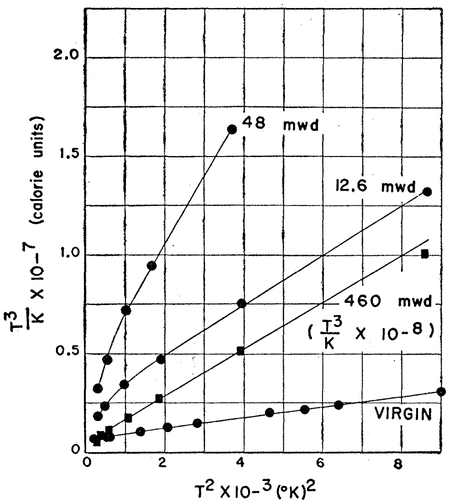

FIG. 6. The function $T^3\kappa^{-1}$ *vs* T^2 for AGOT–KC graphite with various neutron exposures. Note change in scale for the 460-Mwd curve.

parameters used are quite approximate and especially since porosity effects have been neglected. Furthermore, for small crystallite sizes, damage is more liable to cause an appreciable warping or buckling of the planes than in larger crystals. This will change the apparent scattering power of the individual defect, i.e., will change the factor g in Eq. (8) which we have assumed a constant. By the same token, such warping of the lattice may inhibit defect migration somewhat which could mean that the smaller crystallites do, indeed, retain more damage for a given exposure. There have not been enough radiation damage studies made of small crystal graphites to permit any definite conclusions to be made concerning the data in Fig. 8.

It should perhaps be mentioned that damage effects on the specific heat itself will not appreciably alter Eq. (8). This is because such specific heat changes will result mainly from bound modes, i.e., modes associated with isolated defects, which have no direct effect on heat conduction.

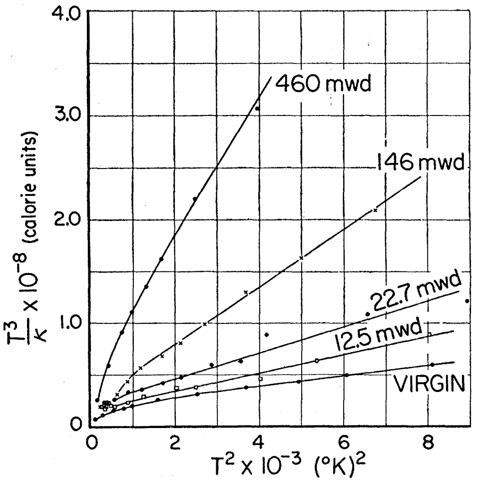

FIG. 7. The function $T^3\kappa^{-1}$ *vs* T^2 for SA–25 graphite with various neutron exposures.

C. Effect of Bromination

The process of forming a brom-graphite compound has been previously discussed (I). Since the residual bromine is thought to be at boundary sites, the only effect of introducing less than about 1% bromine will be to introduce new scattering boundaries or to increase the scattering power of previously ineffective boundaries. Bromine concentrations above 1% cannot be made without appreciably damaging the graphite lattice, which would introduce all kinds of internal defects. If the data in (I) are replotted as $T^3\kappa^{-1}$, it is thus expected that, when considered as a function of T^2, the linear part of the curves will have the same slope for all brominations until about 1% is reached. The slope should then increase greatly. When $T^3\kappa^{-1}$ is considered as a function of T, the slope of the linear part should continuously increase due to the enhanced boundary scattering caused by the bromine. Figures 9 and 10 show these plots and despite a fair degree of scatter, the above expectations are fulfilled in a most gratifying manner. Because of this scatter, however, an attempt to correlate the change of L with the amount of bromine does not seem warranted.

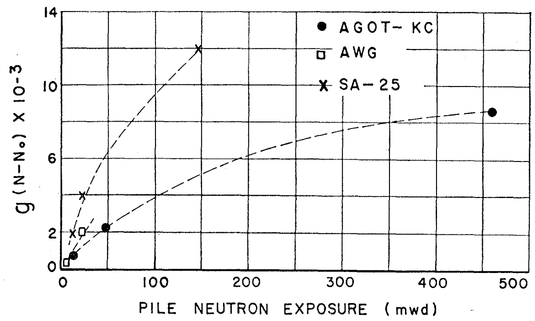

FIG. 8. The relative number of internal defects ($N-N_0$) introduced by neutron irradiation as a function of neutron exposure at about 30°C. The parameter g is an unknown constant.

IV. DISCUSSION

The present work has interpreted the thermal conductivity data of the previous paper (I) on the basis of a two-medium hypothesis. The nongraphitic regions in artificial graphites are assumed isotropic in their conduction properties. By considering these regions to be in series with the graphitic part, a phenomenological expression for the thermal conductivity is derived and it is shown that this formula is entirely consistent, even quantitatively, with all the experimental data presented in (I). Although it is clear that this model, as developed herein, is quite approximate and needs a refining treatment (especially with regard to porosity effects and defect scattering), the order of magnitude agreement with the data is sufficiently good to lend a great deal of confidence in the basic picture.

An alternate explanation of the temperature dependence of the thermal conductivity of graphite has been proposed.[9] By separating the modes of vibration into longitudinal and transverse polarization, it is argued that the transverse mode will be limited by the thickness of the crystallite, while the longitudinal will be limited by the length (usually much greater than the thickness in graphite). On this picture, if the transverse modes are mainly responsible for the specific heat, it is clear that the importance of the longitudinal modes to thermal conduction will be enhanced by the crystallite dimensional ratio. It was further proposed that the longitudinal modes show a specific heat proportional to T^3 at and below 50°K, whereas the transverse modes remain T^2 to very low temperatures. This is based on group-velocity estimates from compressibility data. The conclusion drawn is, of course, that the thermal conductivity will have a temperature behavior between T^2 and T^3 depending primarily on the crystallite-length-to-thickness ratio. The major difficulty which the present authors find in this treatment is the division of the graphite modes into longitudinal and transverse polarizations. This can only be done, even approximately, in special (and unimportant) cases; since the entire method seems critically dependent on the ability to make this division, a serious question arises as to the validity of the interpretation. The further comment may be made that this analysis gives quite bad agreement with some of the observed data. For example, the Canadian natural graphite results show a good T^2 behavior. Assuming, as an extreme case, that the crystallites in the Canadian graphite are as thick as they are long, it can be shown that the crystallite-length-to-thickness ratio for AGOT-KC graphite must be at least 100 to explain the observed temperature dependence on the basis of the above argument. This is the wrong order of magnitude for AGOT graphites whose crystallite dimension ratio is of the order of five. In addition, the observed change in temperature dependence of all types of graphite as the temperature is raised does not appear to conform to what would be predicted from the above model (the prediction is that the function $T^3\kappa^{-1}$ has a negative curvature with increasing T, whereas it experimentally shows linearity breaking into a positive curvature).

As mentioned in the text, recent calculations of the specific heat of graphite have been made by Eatherly and Krumhansl[10] and by Newell.[10] It has been shown that bond-bending force constants are of extreme importance for the out-of-plane and one of the in-plane acoustic modes, in contradistinction to the assumption made by Krumhansl and Brooks.[7] One of the results of this is to make the dispersion of the out-of-plane mode non-Debye-like, i.e., the phonon group velocity is proportional to the frequency in the low-temperature range of interest. Since the specific heat due to this polarization is proportional to T^2 in this range (and is the major contributor to the specific heat), it follows immediately that the thermal conductivity is proportional to T^3. While this news would have been greeted with enthusiasm a year ago by workers in the graphite field, we now know that the best large crystal data show a distinct T^2 behavior and thus that the out-of-plane

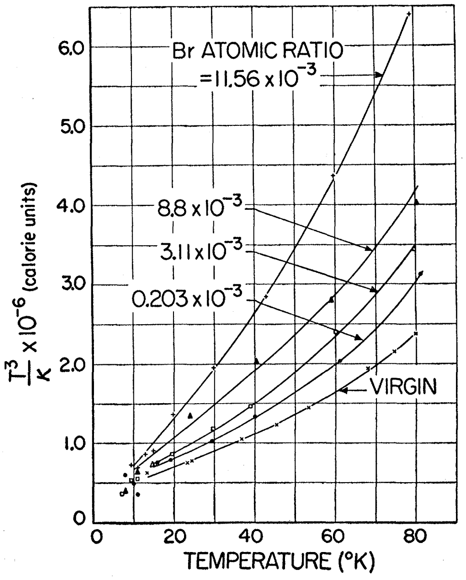

FIG. 9. The function $T^3\kappa^{-1}$ vs T for AGOT–KC graphite with various residual bromine concentrations.

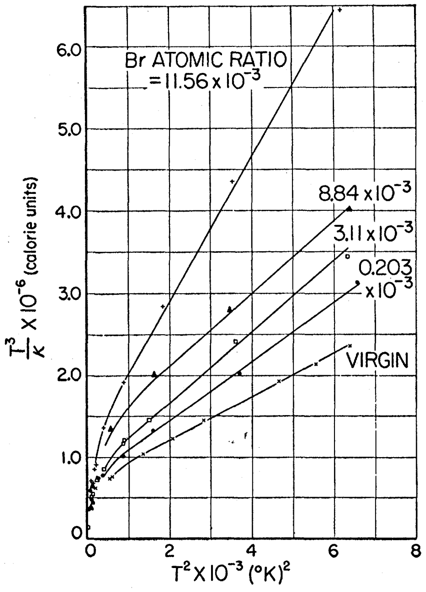

FIG. 10. The function $T^3\kappa^{-1}$ vs T^2 for AGOT–KC graphite with various residual bromine concentrations.

mode cannot contribute significantly to the thermal conductivity. The reason for this probably lies in the magnitude of the group velocity. Unpublished calculations show that at about 20°K, the out-of-plane group velocity is smaller than the softest in-plane mode by a factor of at least 13. This in-plane mode has a constant group velocity, a T^2 specific heat contribution down to very low temperatures and a Debye temperature of about 1600°K. If this mode is the major contributor to the thermal conductivity, the values of the crystallite sizes obtained in the present paper would be wrong by about 50%, which would change none of the conclusions.

ACKNOWLEDGMENTS

The authors wish to express their indebtedness to many people on the staffs of North American Aviation, Inc., and National Carbon Research Laboratories. In particular, we wish to acknowledge many discussions with W. P. Eatherly and J. A. Krumhansl.

PHYSICAL REVIEW VOLUME 104, NUMBER 4 NOVEMBER 15, 1956

Longitudinal Magnetoresistance in the Quantum Limit

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(Received July 12, 1956)

A study has been made of the effect of a magnetic field on the scattering of electrons in a semiconductor with spherical energy surfaces. The theory has been applied to longitudinal magnetoresistance in the case of a very large magnetic field and low temperatures so that all conduction electrons are in the ground oscillator state. Relaxation times for phonon and ionized impurity scattering have been calculated and the corresponding mobilities for a degenerate and nondegenerate semiconductor have been derived. Contrary to the zero magnetoresistance predicted by the usual Boltzmann theory, a field-dependent magnetoresistance is found. For a nondegenerate semiconductor and in the ionized impurity scattering range a negative magnetoresistance is predicted.

I. INTRODUCTION

THE electrical resistivity of a wire is usually affected somewhat by the presence in the wire of a magnetic field. This magnetoresistance may be large or small, and it depends on the nature of the energy band structure of the material, the carrier mobilities, the strength of the magnetic field, and the temperature.

Theories of magnetoresistance are usually based on the one electron band model of solids, and, ordinarily, on a Boltzmann theory treatment of transport. Such theories with various degrees of generality have been given by many authors.[1]

We will concern ourselves here with the result, valid for the most general energy surface and Boltzmann scattering integrals, that for sufficiently high values of a magnetic field the resistance of a wire approaches a limiting value independent of the strength of the magnetic field. The predicted saturation of the magnetoresistance is a consequence of the assumption in most theories that the scattering processes are not much affected by the presence of a magnetic field. This assumption is valid for magnetic fields

$$H \ll mc/e\tau, \qquad (1.1)$$

in which m is the carrier effective mass and τ is the mean free time. This condition may also be written as

$$\omega_0\tau \ll 1, \qquad (1.2)$$

in which ω_0 is the cyclotron resonance angular frequency which is directly proportional to the magnetic field.

On an intuitive basis we might expect that for magnetic fields such that $\omega_0\tau > 1$, the relaxation time may become appreciably dependent on the strength of the magnetic field. For in so strong a magnetic field, the path of the carrier between collisions is very much curved since the period of execution of a complete circular orbit is less than the time between collisions. Thus for $\omega_0\tau \gtrsim 1$, the predictions of the ordinary Boltzmann treatment, which assumes the collisions unaffected by the magnetic field, cannot be trusted without closer examination.

Treatments of electric conduction in strong magnetic fields have been made by Titeica[2] and Davydov and Pomeranchuk.[3] Each of these treatments was somewhat special, but both showed that in magnetic fields for which $\omega_0\tau \gg 1$ there can be noteworthy effects on the magnetoresistance arising from the quantization of the electron orbits. It is such effects that we wish to discuss in the following work.

The theory of Titeica concerned the resistivity of a good metal in which the chief mechanism of scattering

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[1] J. McClure, Phys. Rev. **101**, 1642 (1956). This reference contains references to other relevant work.

[2] V. S. Titeica, Ann. Physik **22**, 129 (1935).

[3] B. Davydov and I. Pomeranchuk, J. Phys. (U.S.S.R.) **2**, 147 (1940).