THERMAL CONDUCTIVITIES OF POLYCRYSTALLINE CARBONS AND GRAPHITES*

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The dependence of the thermal conductivity $K$ of polycrystalline carbons and graphites on the mean crystallite diameter $L_a$ was experimentally investigated for ambient temperatures ranging from 100°K to 400°K. The conductivities were determined by the standard method of measuring the temperature gradient established along the axis of a cylindrical specimen by a definite power input. The mean crystallite diameters were determined from the broadening of X-ray diffraction lines. For well-graphitized samples the thermal resistivity, $1/K$, varies almost linearly with the reciprocal of mean crystallite diameter $1/L_a$. For such samples the thermal resistivities can be separated into two parts which correspond to scattering by the boundaries of crystallites and to the mutual lattice-wave scattering. The dependence of the lattice scattering on temperature and the values of the corresponding free paths are obtained by linear extrapolation to $1/L_a \to 0$. For poorly- and non-graphitized carbons the thermal resistivity increases much faster than linearly with increase of $1/L_a$. Possible reasons for the breakdown of Debye's linear relationship are discussed.

1. INTRODUCTION

The thermal conductivity of carbons and graphites has been studied by a number of investigators. A review by Castle\(^1\) contains references to the main publications prior to 1954, a condensation of the results and a discussion of their significance. It must satisfy the Debye relation, that is

$$K = \gamma \rho C \ell \ell,$$

where $\rho$ is the density, $C$ the specific heat for unit mass, $v$ the velocity of the lattice waves transporting the thermal energy, $\ell$ the mean free path for scattering of these waves and $\gamma$ a numerical factor which is usually taken to be equal to $\frac{1}{3}$. In poly-crystalline materials two kinds of scattering processes occur: Scattering by other lattice waves (lattice scattering-mean free path $\ell_L$) and by the boundaries of crystallites (boundary scattering-mean free path $\ell_B$).

In view of the additivity of scattering probabilities, one has

$$1/\ell = 1/\ell_L + 1/\ell_B$$

Since $\ell_L$ increases with decrease of temperature, at sufficiently low temperatures $1/\ell_L$ can be neglected and the mean free path $\ell$ of lattice waves becomes temperature independent and equal to $\ell_B$; that is, approximately equal to the average dimension of crystallites. Thus for sufficiently low temperatures, neglecting the possibility of small variations in the velocity of the lattice waves, $K$ should be proportional to the specific heat $C$. However, it was found by Berman and by Tyler and Wilson (references 1 and 3 in paper by Castle\(^1\)) that at low temperatures the heat conduction of poly-
crystalline graphites increases with temperature faster than does the specific heat. An explanation was proposed by Klemens in which it is assumed that the discrepancy is intrinsic to the graphitic structure and is connected with the shape of graphite crystals. The suggestion of Tyler and Wilson that the discrepancy might be due to an additional scattering at the crystalline contacts led Smith to investigate heat conduction of a single graphite crystal. Smith found that $K$ in the temperature range $5^\circ$ to $35^\circ$K is about proportional to $T^2$, as expected on theoretical grounds to hold in a limited range of temperatures for the specific heat of a two-dimensional lattice structure such as that of graphite.

Several papers have recently appeared in which results of measurements on the specific heat of polycrystalline graphite performed at low temperatures are reported. According to DeSorbo and Tyler, $C \propto T^2$ in the range $T = 13^\circ$ to $54^\circ$K, but more recently Bergenlid et al. found $C \propto T^{1.5}$ around $T = 90^\circ$K and $C \propto T^{2.4}$ between $T = 1.5$ and $12^\circ$K. On the other hand, the results of DeSorbo and Tyler and also those of Bergenlid do not agree well in the lowest temperature range with the work of Keesom and Pearlman, who found in the lowest temperature range ($1^\circ$ to $2^\circ$K), $C = aT + bT^3$, the linear term being interpreted as the specific heat due to the conduction electrons and holes and the cubic term as the lattice specific heat; for somewhat higher temperatures Keesom and Pearlman find $C = aT + cT^2 - d$ and above $T = 10^\circ$K, $C = eT^2 - f$. These disagreements in specific heat values are, however, relatively small and it seems quite certain that in this range the heat conduction increases faster with temperature than the specific heat. Unfortunately different investigators used samples of polycrystalline graphite of different origins and of an unspecified average crystallite size and type of carbon so that essentially all the results are not exactly comparable. Furthermore the temperature variation of the velocity $v$ has not been determined and consequently one is not sure what the extent of the deviations in temperature dependence between $K$ and $C$ actually is. It would seem that if there are any deviations caused by the polycrystallinity of the material, the deviations should become more pronounced as the crystallite size becomes smaller. A systematic study of the heat conduction in a wide temperature range using carbons with well-controlled crystallite sizes seems imperative not only in order to test the general predictions as they were discussed in Castle's paper, but to disentangle the different factors involved. The work reported below represents the first step in this direction. It is gratifying to see that although these investigations cover a relatively narrow temperature range a considerable amount of information about different factors can be extracted from the results. It is hoped that an extension of this work to lower and higher temperatures will bring about a better understanding of the mechanism of heat conduction in polycrystalline materials in general and for carbons in particular.

II. APPARATUS AND EXPERIMENTAL PROCEDURES

A. Preparation of Samples

A mix was prepared which consisted of 100 parts of Kendall coke (soft type car-
bon), 42 parts of medium grade coal tar pitch and 2 parts of Socony Vacuum Oil Co. Vacwax 80 as "extrusion oil." The coke was "calcined" to 1100°C, crushed into powder using a roll-mill and passed two times through a small Raymond mill. A range of particle sizes from very fine flour to a powder just able to pass through a No. 50 Tyler sieve was obtained. The mix was extruded through a ½ inch die and cut into 6-inch-long sections. The rods so obtained were baked, a period of five days being used to reach the top temperature of 1100°C. Subsequently the rods were heat treated to various temperatures as required, in a graphitizing furnace using a nitrogen atmosphere to prevent oxidation. The temperature was determined by means of an optical pyrometer. In each heat treatment, the rods were soaked at the maximum temperature for about five minutes. After each heat treatment a small amount of the carbon was scraped from the ends of the rod for X-ray studies. The apparent density of each rod was checked before and after baking and after each heat treatment.

B. Measurements of Crystallite Sizes

Since most of the heat conducted through carbons and graphite is transported along the graphitic planes, the crystallite dimension of the greatest interest is the diameter of the crystalline planes or the so-called $L_a$ dimension. The $L_a$ dimension was determined from the broadening of the X-ray diffraction lines; as usual the procedure followed in the determination of $L_a$ for the non-graphitized carbons differed somewhat from that for graphites. The $L_a$ dimension can be calculated from the broadening of X-ray diffraction lines by means of the formula $L_a = \alpha \lambda / B \cos \phi$ where $\lambda$ is the wavelength of the X-ray used, $\phi$ the angle of incidence of the X-rays on the sample, $B$ the full width of the X-ray diffraction line at half intensity and $\alpha$ a constant. $\phi$ and $B$ are expressed in radians. It has been shown by Warren\textsuperscript{8} that for the non-graphitized carbons, when $L_a$ is being determined from the broadening of two-dimensional diffraction lines, $\alpha$ has to be taken as equal to 1.85. The line used for this purpose in this work was the 10 line; for graphites the three-dimensional 110 line was used, in which case $\alpha = 1.00$.

The shape of the diffraction lines was obtained by using the "fixed count" method with a North American Philips X-ray counter spectrometer. Copper $K\alpha$ radiation filtered through nickel was used. The "half widths" obtained from the diffraction lines were corrected for the three following effects:

1. Some broadening of the lines results from finite slit widths, scattering of X-rays in air and from penetration of the X-rays into the sample because of the weak absorption of X-rays by the carbon material. The total broadening from these three sources was corrected for using a method outlined by Jones.\textsuperscript{9} A sample composed of very large (effectively infinite) graphite crystallites was used to determine the broadening not due to diffraction effects. Ceylon graphite was used for this purpose. Correction curve "a" from Jones' paper was then used to determine the correct diffraction width. Curve "a" was decided on in preference to the curve "b" given by Jones because it gave consistent results for the most highly graphitized samples when a number of different slit width combinations were used so that different instrumental broadenings had to be corrected for. This correction turned out to be considerable only for the well-graphitized samples.

2. Some error in half width is introduced because of failure to resolve the $K\alpha_1$ and $K\alpha_2$ peaks.\textsuperscript{8,9}  

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\textsuperscript{8} B. E. Warren, Phys. Rev. 59, 693 (1941).

C. Measurements of Thermal Conductivity

The thermal conductivities were determined by the standard method of measuring the temperature gradients set up along the axis of a long cylindrical rod by a definite power input. The apparatus is shown in Fig. 1.

A heat coil made from nichrome wire was wound at the middle of the rod. The temperature gradients on each side of the heater were determined by means of chromel-constantan thermocouples whose junctions were pressed into small shallow holes drilled in the samples at the positions marked "X". Three thermocouples were used on each side of the heater to check the linearity of the temperature variation along the sample. The thermal emf's at the four bath temperatures used were found to agree with the values given in tables published by the National Bureau of Standards.\(^\text{10}\) The thermal emf's were determined using a type K potentiometer which was sensitive to 1 $\mu$V in the circuit used. The differences in thermal emf between the first and third thermocouples were always greater than 200 $\mu$V. As a general check, the samples were run first with a definite arrangement of the thermocouples and then again with the thermocouples interchanged. The differences between the results of such runs were of the same order as the maximum scattering of results for one arrangement, that is, less than 5% in conductivity.

The whole chamber was evacuated to make sure that all the power introduced into the heater coil flows out to the ends of the sample. The sample heater coil was much hotter than the sample itself because of poor thermal contact. To prevent excessive heat loss from the heater, a small radiation shield made of brass tube with two brass rings, cut longitudinally into two parts was clamped tightly around the center part of the sample so that it enclosed the heater coil. A large radiation shield was made by cutting a plastic cylinder longitudinally into two parts. The sample was then clamped

between these two sections and another heater coil was wound around the middle of the radiation shield. Power was supplied to this heater coil in order to equalize the temperature gradients along the shield to those along the sample. A differential thermocouple with one junction touching the surface of small shield and the other touching the inside of the radiation shield, at points indicated by “XX”, indicated the equalization of the gradients.

In order for the chamber to be easily assembled and disassembled and have the vacuum seals hold over the range of temperatures used, a gasket made of soft solder was clamped between the flanges, as shown in Fig. 1. The bolts were passed through iron spacers so that as the chamber was cooled the relative contractions were such that the gaskets were clamped more tightly.

One end of the sample and radiation shield holder was pressed in direct thermal contact with the end of the chamber and the other end was in contact indirectly by means of a section of braided copper. A stiff coil spring maintained the direct contact in spite of thermal contractions.

Checking on the effects of radiation losses, it was found that for the least conducting sample (1200°C heat treatment), a change of three per cent in the shield gradients caused a change of one per cent in the sample gradient.

The whole chamber was immersed in baths of respectively boiling water, melting ice, dry ice in acetone and liquid nitrogen.

Because of oxidation, each heat treatment resulted in a small decrease in density of the rods. All the results have been recalculated for a common density of 1.49 g/cm³. The density correction was obtained by comparing the thermal conductivities for two samples of slightly different densities which had been simultaneously heat treated to the same temperature. The corrections turned out to be small in all cases.

III. RESULTS AND DISCUSSION

A. General Results

The thermal conductivities as obtained for different rods and for different heat treatments are plotted in Fig. 2 as a function of ambient temperature. One can see here the transition from the characteristic temperature dependence for well-graphitized samples with a maximum of conductivity around the room temperature to an almost

![Fig. 2. Heat conductivities K of Kendall coke carbon rods heat treated to different temperatures as a function of ambient temperature.](image)

<table>
<thead>
<tr>
<th>HT, °C</th>
<th>(L_a), Å</th>
<th>(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>115°K</td>
<td>205°K</td>
</tr>
<tr>
<td>1200</td>
<td>0.0165</td>
<td>0.0369</td>
</tr>
<tr>
<td>1350</td>
<td>0.0228</td>
<td>0.0478</td>
</tr>
<tr>
<td>1500</td>
<td>0.0387</td>
<td>0.075</td>
</tr>
<tr>
<td>1750</td>
<td>0.061</td>
<td>0.128</td>
</tr>
<tr>
<td>1950</td>
<td>0.110</td>
<td>0.220</td>
</tr>
<tr>
<td>2100</td>
<td>0.172</td>
<td>0.331</td>
</tr>
<tr>
<td>2200</td>
<td>0.245</td>
<td>0.470</td>
</tr>
<tr>
<td>3000</td>
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<td>0.650</td>
</tr>
<tr>
<td>3100</td>
<td>0.500</td>
<td>0.900</td>
</tr>
<tr>
<td>1050</td>
<td>1.18</td>
<td>1.80</td>
</tr>
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</table>
One can see from Table I, that for the lowest ambient temperature a change in crystallite size by a factor of about 8 (290/37) results in an increase in conductivity by a factor of 30. Now $\ell_n = L_n$, since the conduction takes place mainly along the graphitic planes. One can see, therefore, that a serious deviation from the proportionality of $K$ with $\ell_n$ required by the Debye formula (1) for low temperatures is present. Actually the deviation is even greater than this since the mean free paths are not equal to $\ell_n$'s, but are slightly smaller (eq. (2)). In order to see the character of these deviations it is convenient to rewrite eq. (1) in the form

$$ CR = 1/\gamma_L \rho \nu L_{\perp} + 1/\gamma_R \rho \nu L_n $$

where $R$ is the thermal resistivity and two different $\gamma$'s are introduced for reasons to be explained later. The equation (3) means that $CR$ plotted as a function of $1/L_n$ should yield a straight line for each ambient temperature. In Fig. 3 the values of $1/K$ taken from Table I and multiplied by corresponding values of specific heat taken from the data of Magnus are plotted as a function of inverse crystallite diameter. An approximately linear relationship is obtained only for large crystallite sizes, the values of $CR$ for small crystallites being very much greater than the expected ones and increasingly so as the crystallite size diminishes.

One could object to the general use of the specific heat of graphite for all carbons on the ground that the specific heat might be dependent on the crystallite size. Unfortunately, this question has not yet been experimentally investigated.\(^{12}\) As Stratton\(^{12}\) has shown, there are reasons to expect that the specific heat for fine polycrystalline materials might differ slightly from the

\(^{11}\) A difference in specific heat was found between activated charcoal and graphite by F. Simion and R. C. Swain, Z. Physik. Chem. B, 28, 189 (1935).

\(^{12}\) R. Stratton, Phil. Mag. 44, 510 (1953).
specific heat of single crystals due to the presence of surface terms in the energy expression. However, percentage-wise, important differences in specific heats are expected only at low temperatures and for small crystallite sizes, that is, in the region where the deviations are so great that the corrections would not materially affect the general shape of the curves in Fig. 3 anyway. Consequently all the conclusions reached below will hold irrespective of the exact values for the specific heat of carbons.

B. Polycrystalline Graphite

The section of Fig. 3 corresponding to large crystallite sizes is replotted on a larger scale in Fig. 4. One can see that the linear relationship between CR and 1/Lₐ is really not obeyed even for quite large crystallite diameters. Although straight lines are drawn through the pairs of experimental points corresponding to the largest diameters determined, one has to admit that some curvature might still be present even here and consequently the crossings of these straight lines with the CR-axis might lead to rather too low than too high values for the product CR extrapolated to the infinitely large crystals. It would be very gratifying to have some experimental points on the graph located at lower 1/Lₐ; unfortunately determinations of the crystal diameters greater than 300 Å seem to be too inaccurate to permit a reliable check on the linearity of the curves at great Lₐ. It seems rather that the procedure could be reversed and by fitting the CR values taken at several temperatures into the graphs very great crystallite sizes could be estimated: This was actually the way the crystallite size given in the Table I for the 7 1/2° C sample was obtained.

From the values of CR obtained by extrapolation, the mean free paths corresponding to the lattice scattering alone can be obtained from equation (3), by noting that CR₁ = 1/(γₗᵥLₐ). One finds

\[ CR₁ \approx \frac{(CR₁ - CR_{∞})Lₐ}{CR_{∞}} \]

that is, an absolute value for the mean free path Lₐ is obtained directly from the graph up to the unknown factor γₗᵥ/Cₗ. The values of γₗᵥ/L₉ᵦL so found are plotted in the upper part of Fig. 5 as a function of temperature T. As will be explained below, γₗᵥ > γₗ at low temperatures; when the temperature is increased, γₗᵥ → γₗ. Taking the very roughly estimated values of the ratio γₗᵥ/γₗ from the slopes (see below) the broken curve is obtained for 1/L₉ᵦ. This curve is actually the curve of CRₗᵥ multiplied by a factor to fit the scale.

One can see from Fig. 5 that the lattice scattering (inverse mean free path 1/L₉ᵦ) increases faster than linearly with temperature; this is what had to be expected, since due to the linearity of the specific heat in this temperature region according to
Fig. 5. Temperature dependence of the inverse mean free path for lattice scattering $1/\ell_L$ as estimated by extrapolation of the results Fig. 4 (upper insert) and by using data of Powell and Schofield (main curve from 400°K up).

Debye has shown that above the Debye temperature $\Theta$ the lattice scattering is proportional to the absolute temperature. Peierls has discussed the scattering at temperatures below $\Theta$ and shown that at sufficiently low temperatures

$$1/\ell_L \sim \kappa T + \lambda T^e e^{-\theta/2T},$$

where the linear part is due to lattice defects and the exponential part to the mutual interaction of acoustical waves. In Fig. 5 a well-developed straight-line section is present for $T > 1600°K$ so that it seems that the average Debye temperature corresponding to the lattice scattering is $\Theta \approx 1500°K$. Since the heat is transported by both longitudinal and transverse vibrations along the graphite plane, this value seems to be of the right order of magnitude. At low temperatures the dependence is definitely not purely exponential; it might be a combination of a linear and exponential term, or might be more complicated. With all the possible errors of extrapolation, it is impossible to decide as to the exact shape of the curve. It is clear, however, at this stage that there is a definite contribution from lattice imperfections. The lattice imperfections involved are undoubtedly those which had no time to diffuse out and were frozen-in in the graphite crystallites when the material was cooled at the end of the heat-treatment process. Consequently a strong dependence of the shape of the low temperature part of the curve, Fig. 5, on the method of cooling the graphite should be expected. It is also clear that since the lattice scattering does decrease about linearly

2900°K are plotted in Fig. 5. The decrease above 2500°K is due either to a contribution from the electronic conduction or to the radiative conduction through the pores and will not be considered further.

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with temperature, in all discussions on
the disagreement between the temperature
dependence of \( C \) and \( K \), before the compari-
on is made, the latter should be corrected
ting down to the lowest for lattice scattering
for carbon and graphite. (see Fig. 6).

In order to find the velocity of the waves
responsible for the heat transport from the
slopes of the straight lines, Fig. 5, the resis-
tivity values \( R \) have to be corrected for
temperature, high value could be a lower limit.

Actually \( \gamma_b \) is about equal to \( \gamma_L \) (and
consequently equal to about \( \frac{1}{2} \)) only when
the accommodation coefficient \( \alpha \) at the
boundaries is equal to 1. If the heat travel-
ing through the lattice is scattered at the
boundaries so, that the distribution of
energy among vibrational modes in the
scattered waves corresponds to the local
temperature at the boundary, then (by
definition) the accommodation coefficient
is equal to one. However, when the waves
are just reflected by the boundaries, the
accommodation coefficient is zero, and the
heat transport from one end of the crystal
to the other will be slightly greater (\( \approx 2/\pi \)).

Moreover, if two crystals are joined at the
boundary by direct valence bonds an in-
coming wave will set the common boundary
vibrations. Consequently for \( \alpha < 1 \) a
fraction of waves through the second crystal
will possess a distribution of modes corre-
sponding to a higher temperature than the
temperature of the crystalline contact from
which they originate. Thus the heat con-
duction will be increased. One can easily
show that for the conduction across in-
finity long crystalline strips of the width
\( L_a \) in the direction of the width \( 1/\gamma_b =
\pi/2 \cdot t \cdot [1 - (1 - \alpha)^2] \), where \( t \) is the fraction
of nonaccommodated modes which passed
into the second crystallite strip. When two
crystals are joined directly, it seems reason-
able to assume that \( t \leq \frac{1}{2} \). When they are
separated by a few disorganized carbon
atoms, \( t \) will become smaller. On the other
hand, the accommodation coefficient must
increase with temperature, since there are
more modes excited and there are more
interactions leading to accommodation.

Taking for the lowest temperature used in
this work arbitrarily \( \alpha = \frac{1}{2} \) and assuming
quite good bonding (\( \ell = \frac{1}{3} \)) one estimates
\( \gamma_b \approx 0.8 \gamma \) and \( v \approx 15,000 \text{ m/sec} \), what
agrees well with the average Debye tem-

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14 S. Mrozowski, This volume, page 203.
15 The consideration of the \( z \)-factor in calcula-
tion of \( \ell_L \) was not necessary since the factor
cancels out in Eq. (4).
In Fig. 6, the product $CR$ is plotted as a function of temperature for highly graphitized samples. Down to $115^\circ K$ the behavior is normal, the curves tending toward a limiting value $(CR_B)_{T=0} = 1/(\gamma_B v)\rho L_a$, and does not give any indication of the upward trend incipient below $60^\circ K$. The lowest curve was calculated using the data for the specific heat by DeSorbo and Tyler and for the conductivity by Tyler and Wilson (Sample A). When the Tyler and Wilson data are corrected for the density and fitted into the graph Fig. 5 an average crystal diameter of $900\AA$ is found for their graphite Sample A. Subtracting the lattice scattering from each of the curves in Fig. 6 a set of corresponding $CR_B$ curves is obtained. All three curves show the same relative temperature dependence as expected (the temperature dependence being due to $\gamma_B v$). One might comment here that the observed strong temperature dependence of $\gamma v$ plus the lattice scattering correction make the discrepancy between the temperature dependence of $C$ and $K$ at lower temperatures even greater than suspected.

C. Polycrystalline and Amorphous Carbons

The thermal resistivities of carbons greatly exceed the values expected by extrapolation of the linear trend observed for large crystallites (See Fig. 3). The deviation from linearity cannot be due to a size dependence of the factor $\gamma_B$ since $\gamma_B$ depends mainly on the nature of the intercrystalline bonding. If one assumes that the deviation is due to an additive extra resistance $R_I$, this resistance can be estimated from Fig. 3 and plotted as a function of temperature (Fig. 7). It turns out that this resistance $R_I$ is strongly decreasing with increase in temperature and increasingly so, as the crystallite size decreases. One can try to interpret this resistance as resistance due to the disorganized carbon phase present between the crystallites.
It seems that even without the disorganized phase, the boundaries between crystallites should present some kind of barriers to the transmission of heat. The crystallites being bonded at the peripheries by randomly distributed C—C bonds, the transmission of vibrations should become more effective as the temperature increases (shorter wavelengths). If one includes the disorganized carbon phase as part of the barriers one can say in general that the curves Fig. 7 give the variation of the opacity of the barriers to the flow of the accommodated flux, as function of temperature.

On the other hand, one might consider $\gamma_B$ minus the part of $\gamma_B$ due to change in $\gamma_B$ as the resistance of the disorganized layers to the flow of accommodated flux, that is consider the conduction as occurring through a two component medium (crystallites dispersed throughout an amorphous phase), the resistance of the amorphous phase decreasing strongly with increase of temperature.

For the smallest crystallite sizes ($L_a \leq 40 \text{ Å}$) such a two component interpretation is objectionable in view of the assumed additivity of the resistances. The splitting is obtained by extrapolating the linear relation (3) to low crystallite sizes and it seems questionable if any meaning can be attached to such a large extrapolation. When the mean free path becomes of an order of one or even several wavelengths, the concept loses its usefulness because it becomes impossible to speak about travelling waves, inside such small systems as carbon crystallites. This is true a fortiori for amorphous substances. A mean free path of an order of several interatomic distances means that the normal vibrations of the system cannot be decomposed into travelling waves, thus the free path does not have the necessary directional qualities. The interaction between different vibrational modes of a small crystallite hooked to its neighbors through $\gamma_B$ becomes a constant ($\alpha = 1$).
Fig. 8. Schematic drawing representing the general trend of the variation of the product $CR$ as a function of inverse crystallite size from large crystallite sizes down to amorphous material. Broken line fitted according to Eq. (3). Circle at crossing gives the apparent $l_B$ ($L_m$) value if one uses Eq. 1 for the amorphous material.

the disorganized phase is so strong that the mean free path calculated from Eq. (1) does not have to be in any direct relation to the dimensions of the crystallite.

For these smallest crystallites sizes the curves Fig. 3 show a slower rise: This is as expected since all curves should level off, tending to a limiting value $CR_\lambda$ for a perfectly amorphous material. An extension of the straight line relationship found for large crystallites (or of the same relationship but with $\gamma_B = \frac{1}{2}$) will lead to a crossing with the $CR$ curve. The value of $L_m$ for which this will occur will have, however, no relation to any actual dimension in the system (See Fig. 8). One can look at the same problem from another angle: In such fine polycrystalline or amorphous materials waves are so strongly damped that there is not very much point to speak about their velocity; what is observed is the diffusional velocity of the transport of energy. With a so-redefined velocity, Eq. 1 might yield free paths directly related to the dimensions in the microstructure. But no matter which point of view is adopted, Eq. 1 becomes a relation which cannot be subjected to an experimental test.

In conclusion, it seems to the authors that the shape of the $CR$ curve in Fig. 8 might not only be characteristic of carbons, but might in general correspond to the transition from well-crystallized to amorphous material and furthermore, that although the Debye relation explains well the mechanism of heat conduction in the well-crystallized materials, no satisfactory explanation exists at present for the intermediate and amorphous substances.

The X-ray spectrometer used in this work was obtained with the assistance of a grant from the Research Corporation.