THE SPECIFIC HEAT AND THERMAL CONDUCTIVITY OF GRAPHITE

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Summary

The specific heat of graphite is discussed in terms of a modified Debye treatment. It is shown that the contribution from the longitudinal waves varies as T^3 below 45 °K, and as T^2 at higher temperatures, whereas the usual two-dimensional treatment leads to a T^2 variation at all low temperatures. Similarly the transverse contribution varies as T^3 at lowest temperatures, but above 10 °K it varies as T^2.

The temperature variation of the thermal conductivity differs from the variation of the specific heat, even though the thermal resistance arises from boundary scattering. This is explained in terms of a mean free path for waves in the hexagonal plane, which is considerably larger for longitudinal than for transverse waves, resulting in an increased contribution of the former to the thermal conductivity.

I. INTRODUCTION

The specific heat of graphite at low temperatures is observed to vary as T^n, where according to Gurney (1952) $n \simeq 2$ above 25 °K, and according to Berman (1952), quoting unpublished results of Bergenlid and Hill, $n \simeq 2 \cdot 2$ from 8 to 20 °K. The thermal conductivity, measured by Berman (1952) for a number of different polycrystalline samples from 3 °K upwards, is observed to vary as T^n, where n ranges from $2 \cdot 5$ to $2 \cdot 7$ in the temperature range 3–40 °K. At these low temperatures the thermal resistance is due to scattering of lattice waves by the boundaries of the crystallites.

That the specific heat should vary as T^2 instead of T^3, as is the case for most solids and follows from the usual Debye theory, has been explained by Komatsu and Nagamiya (1951) and by Gurney (1952) in terms of the weak binding between the hexagonal layers. They assume that each layer can be treated separately as a two-dimensional crystal, leading to a T^2 variation. The validity of this treatment will be confirmed, and it will be shown that it breaks down at sufficiently low temperatures.

The thermal conductivity has been interpreted by Berman (1952) in terms of the general theory (Klemens 1951 ; Berman 1953). Heat transport is mainly by lattice waves, and the thermal conductivity of each crystallite, with the resistance arising from boundary scattering, should be of the form

$$\varkappa = \tfrac{1}{3} S v L, \quad \dots\dots\dots\dots\dots\dots\dots\dots \textbf{(1)}$$

where S is the specific heat per unit volume, v the wave velocity, and L a mean free path determined by the crystal dimensions. The thermal conductivity

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should thus have the same temperature dependence as the specific heat. If there are other scattering processes, $\varkappa$ should vary with T more slowly than S, a phenomenon frequently observed with dielectric solids (Berman 1953). Graphite appears to be anomalous, because $\varkappa$ increases with T more rapidly than does S. This can be explained by considering the parts played by the waves of different polarization.

II. SPECIFIC HEAT OF GRAPHITE

Graphite is a layer structure, the atoms in each layer being arranged in a hexagonal array with interatomic distance of $a_0 = 1\cdot4$ Å, the separation between these sheets being $a_3 = 3\cdot4$ Å. This anisotropy of lattice spacing results from an anisotropy of binding. The bonds between atoms in each hexagonal layer are covalent, reinforced by the bonding of the fourth valency electron, which is partly homopolar and partly metallic. There is thus strong binding in the hexagonal plane, while neighbouring layers are weakly bound by van der Waals forces.

Thus the frequency ω of the lattice waves, a function of the wave-vector $\mathbf{k}$, will depend strongly on k_0, the projection of $\mathbf{k}$ on the hexagonal plane, and only weakly on k_3, the component along the hexagonal axis. In addition, the maximum value of k_3, being $\pi/2a_3$, is smaller than the maximum value of k_0 by a factor of about $2\cdot8$.

It will be assumed that ω is given by

$$\omega = c_0 k_0 + c_3 \mid k_3 \mid, \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

where c_0 is considerably larger than c_3. While (2) is not likely to be the correct expression for ω, it does represent the general characteristics of the dependence of ω on $\mathbf{k}$ sufficiently well for the present discussions.

The specific heat per unit volume is given by the following integral over the first zone.

$$S = \sum_j S_j = \sum_j \int \frac{\hbar\omega}{(2\pi)^4} \frac{e^{\hbar\omega/2\pi KT}}{(e^{\hbar\omega/2\pi KT}-1)^2} \frac{\hbar\omega}{2\pi KT^2} \, d\mathbf{k}, \quad \dots\dots \quad (3)$$

the summation being over all polarizations. Consider separately a single mode of polarization. Writing $x = \hbar\omega/2\pi KT$, $y = hc_3 k_3/2\pi KT$, $\theta_0 = hc_0/\sqrt{3}a_0 K$, $\theta_3 = hc_3/4a_3 K$; and noting that

$$d\mathbf{k} = 2\pi k_0 dk_0 dk_3 = 16\pi^4 \frac{K^3 T^3}{h^3 c_0^2 c_3}(x-y) dx dy, \quad \dots\dots\dots \quad (4)$$

S_j can be expressed as

$$S_j = 4\pi \int_0^H dy \int_0^{\theta_0/T} dx \, K x^2 \frac{e^x}{(e^x-1)^2}(x-y)\frac{K^3 T^3}{h^3 c_0^2 c_3}, \quad \dots\dots \quad (5)$$

where

$$\begin{aligned} H &= x, & \text{if } x < \theta_3/T, \\ &= \theta_3/T, & \text{if } x > \theta_3/T. \end{aligned} \right\} \quad \dots\dots\dots\dots \quad (6)$$

In other words, if $f(x)dx$ is the number of normal modes in the (reduced) frequency interval x, dx, then $f(x) \propto x$ for $\theta_3/T < x < \theta_0/T$, as correctly deduced by Komatsu and Nagamiya (1951). But if $x < \theta_3/T$, $f(x) \propto x^2$, whereas these authors, incurring

an algebraic error, stated that $f(x) \propto x$ even at lowest frequencies. We have assumed in (2) that the surfaces of constant frequency are cones or truncated cones, while Komatsu and Nagamiya assume ellipsoids of revolution or truncated ellipsoids. But this should not alter the conclusion derived here that $f(x) \propto x^2$ at lowest frequencies—the only alteration being in the region of transition from x to x^2 dependence.

It follows that for $T > \theta_3$ the important values of x are always larger than the permissible values of y; in that case $x - y \sim x$, and

$$ S_j = \frac{4\pi K^4 \theta_3 T^2}{h^3 c_0^2 c_3} \int_0^{\theta_o/T} \frac{x^3 e^x}{(e^x - 1)^2} dx, \quad \cdots \cdots \cdots \cdots (7) $$

so that $S_j \propto T^2$ for $\theta_3 < T < \theta_0$. On the other hand, if $T \ll \theta_3$, the limit of the y-integration in (6) is $H = x$, and $S_j \propto T^3$. Since the maximum value of the integrand is in the vicinity of $x = 4$, deviations from the T^3 law will appear above $\theta_3/4$.

The validity of the two-dimensional model, as used by Komatsu and Nagamiya (1951) and by Gurney (1952) is thus confirmed, except for the lowest temperatures, where the T^2 dependence of the low temperature specific heat, derived by these authors, is replaced by a T^3 variation.

The effect of different polarizations must now be considered. For propagation in the hexagonal plane we must separately consider the following three modes : one longitudinal mode, denoted by I, and two transverse modes. Of the latter, one mode, denoted by II, is polarized in the plane, and one, denoted by III, is polarized perpendicular to the plane. It is expected that $c_0^I > c_0^{II} > c_0^{III}$. For propagation along the hexagonal axis, modes II and III are equivalent and will be denoted by II ; again one expects $c_3^I > c_3^{II}$, but the ratio of these velocities is different from the corresponding ratio for the 0-direction. For intermediate directions, we assume (2) to hold for each polarization separately. Defining a mean velocity in the 0-direction

$$ \frac{3}{<c_0>^2} = \sum_j \left(\frac{1}{c_0^j} \right)^2, \quad \cdots \cdots \cdots \cdots \cdots (8) $$

the specific heat above the highest value of θ_3 becomes

$$ S = \frac{12\pi K^3 T^2}{h^2 2 a_3 <c_0>^2} \int_0^{<\theta_o>/T} \frac{x^3 e^x}{(e^x - 1)^2} dx, \quad \cdots \cdots \cdots (9) $$

and it follows from the observed values of S between 25 and 40 °K that $<\theta_0>$, derived from $<c_0>$, is about 1070 °K. Gurney (1952), attributing the specific heat to mode III only, obtained 614 °K for θ_0^{III}.

Komatsu and Nagamiya (1951) have estimated c_3^I, the velocity of longitudinal waves along the hexagonal axis, from the compressibility and, taking account of dispersion, they obtained $\theta_3^I = 180$ °K. Thus S_I should vary as T^3 below 45 °K.

In fact the specific heat of graphite seems to follow a T^2 law down to 20 °K, which can be explained only by assuming that c_0^I is appreciably larger than c_0^{III}, so that even around 45 °K S_I is only a small fraction of S. Furthermore, it must be assumed that c_3^{II} is considerably less than c_3^I, so that $\theta_3^{II} \ll \theta_3^I$ and deviations from the T^2 law appear only at much lower temperatures for the transverse component than for the longitudinal component. It appears from the specific heat evidence that θ_3^{II} cannot exceed 35 °K and may well be even appreciably lower, and that above 45 °K $(S-S_I) : S_I = 3 : 1$, so that $c_0^I : c_0^{III}$ is of the order of $3 : 2$.

III. Thermal Conductivity of Graphite

The fact that below 50 °K the thermal conductivity of graphite varies more rapidly with temperature than the specific heat is now explicable in terms of a relatively larger contribution from the longitudinal waves towards the conductivity. We generalize equation (1) to

$$\varkappa = \sum_j \varkappa_j = \sum_j \tfrac{1}{3} S_j c^j L_j, \quad \dots\dots\dots\dots\dots\dots (10)$$

where L is the mean free path due to boundary scattering. In general L is of the order of the shortest linear dimensions of the crystal. This holds even for waves travelling in a direction such that the distance between boundaries is considerably larger, for the lattice waves are coupled together, with respect to their deviation from equilibrium, by three-phonon interactions conserving the total wave-vector. The role of these processes has been discussed elsewhere in detail (Klemens 1951); they tend to equalize mean free paths. Thus the transverse waves in the 0-direction are strongly coupled to waves in the 3-direction. The graphite crystals are in the shape of thin plates parallel to the hexagonal plane. If L_3 is the thickness of these plates and L_0 their diameter, it follows that for transverse waves in the 0-direction $L_{II} = L_3$.

Now it is well known that the lattice waves of the highest velocity cannot interact with any other lattice waves of higher frequency, but only with those of lower frequency. It was shown by the author that such interactions have a negligible effect on the effective mean free path. In graphite the longitudinal waves in the 0-direction have the highest velocity of all, and they are therefore not effectively coupled to any waves in the 3-direction. Consequently for longitudinal waves in the 0-direction $L_I = L_0$.

Since for crystal plates $L_0 > L_3$, it follows that for conduction in the 0-direction the ratio $\varkappa_I : \varkappa_{II}$ is larger than $c_0^I S_I : c_0^{II} S_{II}$, hence larger than $S_I : S_{II}$. Therefore the temperature variation of the thermal conductivity is higher than that of the specific heat.

To account for Berman's data, and provisionally identifying the overall conductivity with the conductivity in the 0-direction, $L_0 : L_3$ must be of the order of 10 : 1, which does not seem unreasonable. It is significant that Berman, by using (1) and taking $v \sim c_0^I$, obtained values for L which were of the order of magnitude of the diameter L_0 of the crystal plates.

For conduction in the 3-direction where $L_I \sim L_{II} \sim L_3$, $\varkappa_I$ is again enhanced relative to S_I, because $c_3^I > c_3^{II}$, the ratio of these velocities from the specific heat

evidence being not less than $5:1$.   This difference in velocity occurs to a lesser degree in the 0-direction and is unimportant there.   It follows that the temperature variation for conduction in the 3-direction is intermediate between that of specific heat and conduction in the 0-direction.

For crystal plates the directional anisotropy of the conductivity will be of order $L_0 : L_3$.   In a polycrystalline specimen the overall conductivity will be largely governed by the conductivity in the 0-direction.   We have thus a natural explanation for the high temperature dependence of the thermal conductivity of polycrystalline graphite, for the magnitude of the effective mean free path derived from (1), and for the slightly lesser temperature dependence for conduction along the preferred orientation of the C axis.   To explain the temperature dependence of Berman's specimen of smallest crystal size and lowest conductivity, it must be assumed that for these small crystals $L_0 \sim L_3$, so that $\varkappa_I$ is no longer enhanced relative to S_I.

IV. CONCLUSION

This treatment has been confined to a rough estimate of the relevant parameters occurring in the simplified lattice theory of specific heat and thermal conductivity.   In view of the lack of detailed knowledge of the interatomic forces and the uncertain experimental material, there is no point in refining these calculations.   It does appear, however, that the thermal conductivity can be related to the specific heat according to the usual lattice theory, if account is taken of the special features arising from the high anisotropy of graphite. In order to verify this theory, it would be of value to have measurements of the specific heat from 2 to 8 °K, and of the thermal conductivity of a single crystal of graphite.

V. ACKNOWLEDGMENTS

VI. REFERENCES

BERMAN, R. (1952).—*Proc. Phys. Soc. Lond.* A **65** : 1029.
BERMAN, R. (1953).—*Advanc. Phys.* **2** : 103.
GURNEY, R. W. (1952).—*Phys. Rev.* **88** : 465.
KLEMENS, P. G. (1951).—*Proc. Roy. Soc.* A **208** : 108.
KOMATSU, K., and NAGAMIYA, T. (1951).—*J. Phys. Soc. Japan* **6** : **438.**

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