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Atomic Heat of Graphite between 1 and 20°K†

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The atomic heat of pure artificial polycrystalline graphite has been measured between 1 and 4°K and 10 and 20°K. Precautions were taken to ensure that no error was introduced by gas adsorbed on the graphite. Below 2°K the atomic heat can be represented as the sum of a term proportional to T^3 arising from low-frequency lattice waves and a term proportional to T due to electrons: $C=0.0325T^3+0.031T$ millijoules/mole degree. Between 2.25°K and 4.5°K, $C=0.115T^2+0.031T-0.237$ millijoules/mole degree; between 10 20°K, $C=0.208T^2-6.8$ millijoules/mole degree.

I. INTRODUCTION

CONSIDERABLE attention has been given recently to the band structure of graphite[1–3] and to the vibration spectrum of its lattice.[3–10] This lattice is highly anisotropic, being made up of planes of atoms strongly bound together in a hexagonal network, the planes being held together by weak forces of the van der Waals type. The bond length in the planes is 1.42 A, while the distance between planes is 3.37 A. As a consequence, the Brillouin zone is foreshortened in the direction corresponding to wave propagation perpendicular to the planes. The lattice contribution to the atomic heat, C_L, is therefore found[3–6,8,9] to be proportional to T^2 at low temperatures, rather than to T^3, as is the case for ordinary solids. There is disagreement, however, as to whether the T^2 dependence will hold down to 0°K,[3–5] or whether below a few degrees absolute, a T^3 region will be found.[6,8,10] This question has not been settled by the recent measurements of de Sorbo and Tyler,[11] which show that the atomic heat is proportional to T^2 between 13°K (their lowest temperature) and 54°K. One of the purposes of our atomic heat measurements down to 1°K was thus to investigate the temperature dependence of C_L at very low temperatures. Shortly after a summary of this paper was originally submitted for publication, values were reported for the atomic heat of graphite from 1.5 to 90°K.[12] These data agree very well with those reported here in the over-lapping temperature ranges, but they are interpreted by Bergenlid *et al.*, in a way which leads to a rather different temperature dependence than we find. This difference is discussed below in Sec. IV.

In addition, we were interested in finding the electronic contribution, C_E, to the atomic heat. This was calculated by Komatsu and Nagamiya[3] from the band structure described by Wallace,[1] who found a band that is full at 0°K and an empty higher band which just touches the former. Their rough calculation showed that C_E and C_L would be comparable in size at 1°K.

II. EXPERIMENT

The sample was a cylinder of pure artificial graphite, about 4 cm in diameter and weighing about 170 grams, obtained from the Stackpole Carbon Company. Cigarette paper was fastened to the cylinder with glyptal lacquer, and the thermometer wires (phosphor-bronze in the helium range, lead in the hydrogen range) wound thereon and also secured with glyptal. The thermometers were calibrated against the vapor pressures of the respective baths, using the 1948 scale[13] for helium and the NBS formulas[14] for hydrogen. Insulated constantan wire wrapped on the cylinder was used for the heater. The sample was hung in a vacuum can, and the measurements carried out in the manner described previously.[15] The heat capacity of the glyptal, wires, etc., was less than one percent of the total.

Since graphite is an excellent adsorbent, we anticipated that some of the exchange gas introduced into the vacuum can prior to calibration of the thermometers would remain adsorbed on the sample after most of it was pumped away following calibration. Such adsorbed gas would introduce systematic errors in the heat capacity determinations. To estimate the magnitude of these errors, we carried out two preliminary runs. In run *A*, the exchange gas was pumped away for several hours while the sample was being heated and thereby kept at about 5°K. When the system pressure was constant, heating was stopped and the sample came to bath temperature (4.2°K) in less than an hour. The heat capacity was then measured at 4°K and below.

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TABLE I. Atomic heat of graphite.

n	T °K	ΔT deg	C millijoules/mole degree
2	4.392	0.04862	2.049
3	4.391	0.04839	2.059
4	2.990	0.06667	0.891
5	3.023	0.06357	0.935
1	4.257	0.0901	1.982
2	4.333	0.06173	2.079
3	4.366	0.06151	2.087
4	3.995	0.07320	1.753
5	4.045	0.07120	1.802
6	3.755	0.04650	1.467
7	3.793	0.04469	1.526
8	3.406	0.05632	1.210
9	3.445	0.05522	1.234
10	3.092	0.07264	0.9376
11	3.147	0.07021	0.9702
12	2.748	0.07150	0.7168
13	2.805	0.06829	0.7506
14	2.578	0.08606	0.5954
15	2.655	0.07928	0.6464
16	2.200	0.07267	0.3997
17	2.236	0.07350	0.3951
18	1.778	0.07746	0.2420
19	1.838	0.06769	0.2769
20	1.861	0.07199	0.2604
21	1.632	0.09582	0.1956
22	1.681	0.09118	0.2056
23	1.235	0.07909	0.1019
24	1.255	0.07741	0.1041
25	1.246	0.07584	0.1062
26	1.063	0.07868	0.0715
27	1.081	0.07891	0.0713
1	9.20	0.07631	10.83
2	9.24	0.07328	11.27
3	9.27	0.2016	11.09
4	8.96	0.2245	9.96
5	9.14	0.2124	10.52
6	9.52	0.1890	11.84
7	9.70	0.1752	12.87
8	9.89	0.1701	13.14
9	10.48	0.1414	15.88
10	10.65	0.1346	16.64
11	11.06	0.1203	18.63
12	11.18	0.1170	19.14
13	11.74	0.1001	22.39
14	11.89	0.1935	23.17
15	12.08	0.1850	24.24
16	12.80	0.1622	27.68
17	12.97	0.1569	28.62
18	13.10	0.0736	30.53
19	14.00	0.1314	34.16
20	14.12	0.1284	34.97
21	14.16	0.1260	35.64
22	14.94	0.1141	39.40
23	15.05	0.1126	39.92
24	16.42	0.0911	49.45
25	16.50	0.0901	50.02
26	17.36	0.0811	55.65
27	17.43	0.0801	56.36
28	18.34	0.0722	62.58
29	18.42	0.0720	62.77
30	19.33	0.0661	68.47
31	19.40	0.0655	69.15
32	20.30	0.0602	75.20
33	20.36	0.0593	76.49

In run B, the sample was heated in steps up to about 10°K, and the system pressure became constant only after about seven hours of pumping. Heating was then stopped, and the sample did not reach bath temperature until about eight hours later. The heat capacity was measured at several temperatures, and found to be about 10% lower than the values at corresponding temperatures measured during run A. The results reported below were obtained during a third run for which the pumping procedure of run B was followed. In this run and also run B, increasing the sample temperature when the system pressure had finally become constant after prolonged pumping produced no increase in system pressure, thus indicating that substantially all of the exchange gas had been pumped away.

The possibility that air adsorbed on the sample at room temperature might contribute significantly to the measured heat capacity was also investigated. The sample was heated to about 300°C and the gas driven off, less than one cc (NTP), was collected. The corresponding heat capacity below 20°K would be less than 0.1% of the total, as estimated from the data of Morrison and Szasz[16] for N_2 adsorbed on TiO_2.

III. RESULTS

The results of our measurements in the helium range and the hydrogen range are presented in Table I. They are given in graphical form in several different ways in Figs. 1–3. In Fig. 1, we plot C/T *versus* T^2 (left-hand ordinates) and C *versus* T^2 (right-hand ordinates) for the helium range data. Here C is the total measured atomic heat. We also plot in Fig. 1, C_L *versus* T^2, where C_L is the lattice contribution to the atomic heat,

$$C_L = C - C_E, \qquad (1)$$

where C_E is the electronic contribution. This is estimated on the assumption that the straight line obtained below 2°K in the C/T *versus* T^2 plot results from the sum of a term proportional to T^3 (C_L) and a linear term (C_E) whose coefficient is given by the intercept of the line. The equation for the line is

$$C = 0.0325T^3 + 0.031T \text{ millijoule/mole degree.} \qquad (2)$$

The data evidently do not conform to this equation above about 2°K. In the range between 2.25° and the boiling point, the C *versus* T^2 appears to be a good straight line, with the equation

$$C = 0.118T^2 - 0.177 \text{ millijoule/mole degree.} \qquad (3)$$

The straight line fit is improved if C_E is subtracted, resulting in the line labeled C_L, which has the equation

$$C_L = 0.115T^2 - 0.237 \text{ millijoule/mole degree.} \qquad (4)$$

The data between 10 and 20°K are plotted in Fig. 2, in the form C *versus* T^2. A fairly satisfactory fit is found with the line

$$C = 0.208T^2 - 6.8 \text{ millijoules/mole degree.} \qquad (5)$$

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[16] J. A. Morrison and G. J. Szasz, J. Chem. Phys. **16**, 280 (1948).

The data of de Sorbo and Tyler[11] are also plotted in Fig. 2. These data are about 10% higher; the dashed line is that given by de Sorbo and Tyler[11] as fitting their data between 13 and 54°K:

$$C = 0.216T^2 \text{ millijoule/mole degree.} \tag{6}$$

The source of the discrepancy between our results and those of de Sorbo and Tyler[11] is not clear. Their material was in the form of powder, and was contained in a copper calorimeter during measurement. It is unlikely that the difference is a particle size effect, since they give the average thickness of the crystallite plates as 230 A, while x-ray measurements carried out on our sample by Mr. W. D. Derbyshire of this laboratory, using the broadening of the 002 line, give about 300 A. The values reported by Bergenlid *et al.*,[12] are also lower than those of de Sorbo and Tyler[11] below about 25°K.

We will discuss below the analysis of our data in terms of Figs. 1 and 2. In these graphs, the straight lines are drawn solid or dashed where they pass through the points on which they are based, and dotted where they are extrapolated beyond these points. The solid or dashed lines do not deviate from their points by more than the experimental error (about three percent). In order to see whether any single equation of the form $C = aT^n$, [such as Eq. (6) found by de Sorbo and Tyler[11]] would fit our data, we plotted log *C versus* log *T* in Fig. 3. The straight line drawn there, which has the equation

$$C = 0.0605T^{2.38} \text{ millijoule/mole degree,} \tag{7}$$

appears to be a reasonably good fit. However, it deviates from the experimental points by as much as 10% at several temperatures, and so is not to be preferred to the lines in Figs. 1 and 2.

Bergenlid *et al.*[12] presented their data in a log-log plot, but they point out that a single straight line will not fit adequately over their entire temperature range. The smooth curve they draw through the points has a slope of 1.8 at 90°K; the slope increases to 2.4 at 4°K. At their lowest temperatures their points fall near a line with the equation

$$C = 0.06T^{2.4} \text{ millijoule/mole degree,} \tag{8}$$

which agrees with Eq. (7) to within the combined accuracies. The same systematic deviations from the line apparent in Fig. 3 occur as well with respect to the line in their graph.

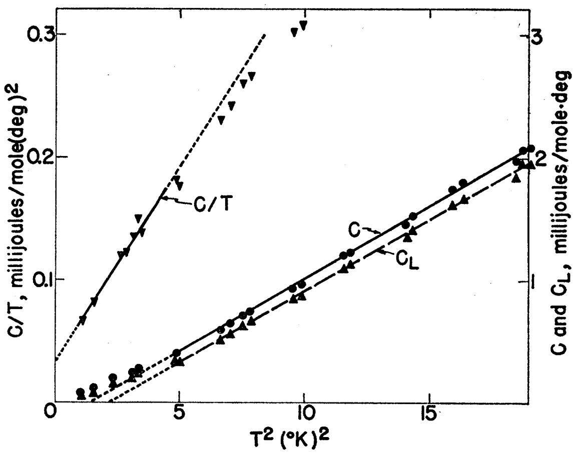

FIG. 1. Atomic heat of graphite below 4°K: ▼ C/T *versus* T^2 (left-hand ordinates); ● C *versus* T^2; ▲ C_L (total atomic heat minus electronic contribution) *versus* T^2 (both on right-hand ordinates).

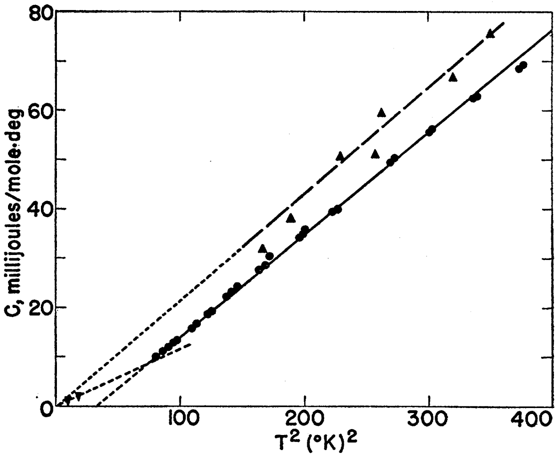

FIG. 2. Atomic heat of graphite *versus* T^2: ▲ de Sorbo and Tyler; ● our data.

IV. DISCUSSION

The temperature dependence to be expected at very low temperatures for C_V of graphite depends on the assumptions made concerning: (a) the temperature dependence of C_L; (b) the presence or absence of a significant contribution to C_V besides C_L, such as an electronic contribution, C_E.

(a) As was mentioned in the Introduction, different theoretical treatments lead to either quadratic or cubic dependence of C_L on T, and it is of course possible that the true temperature dependence differs from both of these. A possible source of evidence to resolve this question might be found in measurements of the thermal conductivity, κ, at low temperatures. It can be shown[17] that

$$\kappa \propto vC_V\lambda,$$

where v is the velocity, C_V the heat capacity per unit volume, and λ the mean free path of the "carriers" of thermal excitation. In graphite heat will be carried mainly by phonons[18] and at low temperatures λ will be limited by the size of the crystallites,[18] and so will not depend on temperature. Since v is also essentially

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[17] P. Debye, *Vortrage uber die Kinetische Theorie der Materie und der Elektrizität* (B. G. Teubner, Leipzig, 1914), pp. 17–60.

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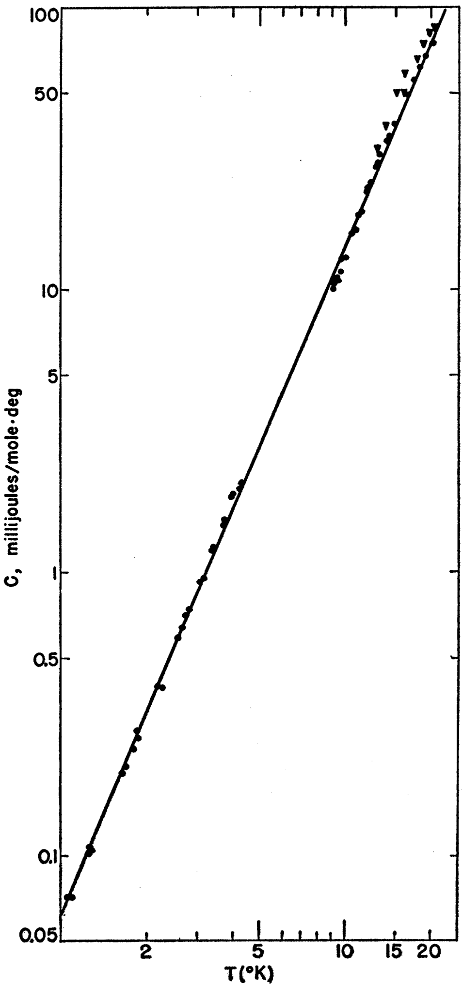

FIG. 3. Atomic heat of graphite below 20°K: ▼ de Sorbo and Tyler; ● our data.

independent of temperature, κ will be proportional to C_L. Hence the results of Berman[18] which show that in graphite κ varies as T^n with n between 2.5 and 2.7 for T between 3 and 40°K, could be interpreted as indicating a similar T dependence for C_L. Klemens,[6] however, attempted to show that this behavior could be reconciled with T^2 variation of C_L by considering the different contributions to κ from the longitudinal and transverse phonons. On the other hand, Smith has suggested[19] that the deviation from T^2 dependence observed by Berman is due to intergranular nongraphitic material in the polycrystalline samples he measured. Smith has recently found[20] that κ is proportional to T^2 for T between 4 and 70°K in samples of natural graphite, thus lending support to this point of view. To sum up, there appears to be no independent evidence concerning the temperature dependence of C_L below 2°K; T^2 dependence would seem likely, at least above 4°K, from Smith's thermal conductivity measurements.

(b) The calculations of Komatsu and Nagamiya,[3] based on Wallace's theory of the band structure of graphite, indicate that in the neighborhood of 1°K the electronic heat capacity might be comparable to that of the lattice. Attempts have been made to correlate the results of measurements[21–25] of the electrical resistivity of graphite with Wallace's theory, with inconclusive results. The theory applies to perfect crystals, while the material available is either polycrystalline artificial graphite or natural crystals of doubtful purity. Attempts to modify it[22,26,27] in order to take these factors into account have not succeeded in improving the agreement with experimental results. On the other hand, Lothar Meyer has reported[28] that new measurements on samples first investigated several years earlier gave results very different from those found originally. He has also found inconsistencies in results on apparently similar samples. This indicates that the discrepancies between Wallace's theory and experimental resistivity values may be due to difficulties in controlling extraneous conditions to which the samples may be very sensitive, such as thermal history, traces of impurities, etc., rather than to defects in the theory itself.[29] Hence these discrepancies between Wallace's theory and the electrical measurements do not in themselves argue strongly against the existence of an electronic contribution to the heat capacity.

On the basis of these considerations, it appears reasonable to conclude from our data that the lattice atomic heat of graphite is proportional to T^3 below 2°K and that there is an additional contribution from the electrons, which is about equal to that of the lattice at 1°K. The electronic term is about three times larger than that calculated by Komatsu and Nagamiya [see Eq. (31) of reference 3]. One of the factors entering into the calculation is the value of the resonance-energy integral involving electrons in adjoining carbon atoms in the hexagonal plane. From the measured C_E we calculate 0.9 ev for this integral, compared with 3 ev, the value used by Komatsu and Nagamiya. The latter value is derived from x-ray emission line fine structure.

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[20] A. W. Smith, Phys. Rev. **95**, 1095 (1954).

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[26] D. Bowen, Phys. Rev. **76**, 1878 (1949).

[27] G. Hennig, J. Chem. Phys. **19**, 922 (1951).

[28] L. Meyer, paper presented December 21, 1953 at the Third International Conference on Low Temperature Physics and Chemistry (unpublished).

[29] It has been brought to our attention that Krumhansl and others have suggested screw dislocations as a possible source for the irreproducibility of conductivity results. These would provide a mechanism for conduction perpendicular to the hexagonal planes without requiring transistors between planes. Unfortunately, no information seems to be available on screw dislocations in graphite.

Coulson[2] has pointed out, however, that the calculation is very sensitive to the shape of the electron level-density curve at the band edge. Since this is not known with great accuracy on the basis of Wallace's theory, it is more likely that this factor, rather than the resonance-energy integral is the source of the discrepancy between measured and calculated values of C_E, and the lack of quantitative agreement between them is not surprising.

Our results are thus in at least formal agreement with any theory which predicts that C_L is proportional to T^3 below a certain transition temperature T_0 and to T^2 at somewhat higher temperatures. Quantitative agreement with any particular theory is hardly to be expected, however, because of the lack of sufficient information about the interatomic force constants which enter.[9,30] It is nevertheless interesting to compare our results with the analysis of Krumhansl and Brooks,[8] which is the most detailed of the treatments of this type.

There are various ways of describing the normal mode atomic displacements in graphite.[3,5,6] Krumhansl and Brooks use the procedure suggested by Lonsdale,[31] according to which the polarization vector of the displacement wave is taken either perpendicular to the hexagonal planes (bending modes; z modes) or in the plane (stretching modes; xy modes). The relatively weak forces between the planes are largely associated with the z modes, while the much stronger intraplanar forces are largely associated with the xy modes. For this reason the z modes will be more strongly excited at low temperatures and hence be the major source of the heat capacity. Therefore Krumhansl and Brooks discuss only these modes in detail.

Using only nearest-neighbor forces, they find that the constant energy surfaces for the z modes in the Brillouin zone are prolate ellipsoids for frequencies much less than

$$2\pi\nu_{1z}=(2S_1/m)^{\frac{1}{2}}, \tag{9}$$

where m is the mass of the carbon atom and S_1 is the restoring force constant between nearest neighbors in adjacent planes. Thus for $\nu \ll \nu_{1z}$ the vibration spectrum for the z modes, $g_z(\nu)$, is proportional to ν^2 as in the Debye continuum approximation, which is known to apply also for real crystals at sufficiently low frequency. As ν approaches ν_{1z} the constant frequency surfaces become flattened near the top and bottom of the Brillouin zone. For $\nu > \nu_{1z}$ they are truncated ellipsoids. Krumhansl and Brooks approximate the behavior of $g_z(\nu)$ in the neighborhood of ν_{1z} by setting it proportional to ν^2 up to ν_{0z} and proportional to ν above ν_{0z}. From the relation

$$\int_0^{\nu_{0z}} \text{const}\times\nu^2 d\nu=\int_0^{\nu_{1z}} g_z(\nu)d\nu=n_zN_0, \tag{10}$$

where $g_z(\nu)$ is their exact analytical expression, (which however is impractical for use in calculating C_L), and N_0 is Avogadro's number, they find $\nu_{0z}=0.9\nu_{1z}$. Then below T_{0z}, the temperature of transition from cubic to quadratic temperature dependence of $C_{L(z)}$, the contribution of the z modes to the lattice heat capacity,

$$\frac{C_{L(z)}}{R}=\frac{8}{3\pi}\cdot\frac{12\pi^4}{15}n_z\left(\frac{T}{\theta_{1z}}\right)^3=66.2n_z\left(\frac{T}{\theta_{1z}}\right)^3=a_3T^3, \tag{11}$$

where

$$h\nu_{1z}=k\theta_{1z}, \qquad T_{0z}\approx 0.3\theta_{0z}; \qquad \theta_{0z}\approx 0.9\theta_{1z}. \tag{12}$$

For T larger than T_{0z} but much less than θ_{mz}, where

$$h\nu_{mz}=k\theta_{mz}; \qquad N_0=\int_0^{\nu_{mz}} g_z(\nu)d\nu, \tag{13}$$

they find

$$C_{L(z)}/R=14.4(T/\theta_{mz})^2-n_z=a_2T^2-a_0. \tag{14}$$

If we interpret our results in terms of these equations, then T_{0z} is about 2°K and θ_{0z} is 6–7°K. In order to calculate θ_{mz} and n_z, some assumption must be made concerning $C_{L(xy)}$ at the lowest temperatures. The value of θ_{mxy} is found by Krumhansl and Brooks from the atomic heat at high temperatures to be about 2500°K. If $C_{L(xy)}$ is proportional to T^2 at the lowest temperatures, it would be equal to $4.61\times10^{-6}T^2R$, since there are twice as many xy modes as z modes. This is one-third the total C_v at 2°K, and almost two-thirds at 1°K, but we observe no such quadratic term between 1 and 2°K. Thus we conclude that $C_{L(xy)}$ will be given by an expression like Eq. (11) below T_{0xy} and like Eq. (14) above T_{0xy}, where T_{0xy} is not less than 2°K. If we assume that the xy mode equal energy surfaces in the Brillouin zone are similar to those of the z modes[32] then there will be a quadratic-linear transition in the vibration spectrum of the xy modes as well, at a frequency

$$\nu_{1xy}\approx\nu_{1z}v_{xy}/v_z, \tag{15}$$

where v_{xy} and v_z are the respective wave velocities for the two types of mode. Since v_{xy} would be expected to be larger than v_z, we would expect T_{0xy} to be larger than T_{0z}. If the velocity ratio in Eq. (15) were small enough so that both $C_{L(xy)}$ and $C_{L(z)}$ contributed significantly to C_L below 2°K, then $C_{L(xy)}$ would still be appreciable, and proportional to T^3, between 2 and 4°K. Since we observe no such cubic term in this region, we assume that below 4°K $C_L\approx C_{L(z)}$ and find from Eqs. (14) and (11)

$$n_z=28.5\times10^{-6}, \qquad \theta_{1z}=7.8°\text{K}; \qquad \theta_{mz}=1020°\text{K}.$$

This value of θ_{mz} is somewhat higher than that estimated by Krumhansl and Brooks (950°K). Their

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[32] It has been pointed out by Newell (unpublished) that this assumption may be grossly in error, since it depends not merely on the geometry of the lattice but also on the interatomic forces connected with the two types of mode.

estimates of θ_{1z} and n_z (60°K, 5×10^{-3}, respectively) are much higher than the values calculated from the experimental data.

Although the experimental error in the measured points is only about 1–2%, a term proportional to T^3 between 2 and 4°K which was as large as 10% of C_L at 4°K would not be inconsistent with the line we have drawn in this temperature region. Taking this as an approximate upper limit for $C_{L(xy)}$ below 4°K, we find, using the relation due to Krumhansl and Brooks,

$$2n_{xy}\approx(\nu_{1xy}/\nu_{mxy})^2=(\theta_{1xy}/\theta_{mxy})^2, \tag{16}$$

that $\theta_{1xy}\approx20$°K, $n_{xy}\approx20\times10^{-6}$.

It should be mentioned that it is also possible to fit the data with the assumption that T_{0xy} is also about 2°K. On this assumption, θ_{1xy} is about equal to θ_{1z} at $\sim7-8$°K, since the latter is not very sensitive to the assumption made concerning $C_{L(xy)}$. The major change is in the n's: n_z becomes 19×10^{-6} and n_{xy} becomes 10×10^{-6}. In either case, the data between 10 and 20°K correspond to a decrease in θ_{mz} in this temperature interval, if it is assumed that θ_{mxy} is roughly constant there. As has been pointed out by Krumhansl and Brooks, this decrease in θ_{mz} is to be expected as a consequence of the existence of peaks in the vibration spectrum[7,9] which are neglected in their treatment.

In order to account for the discrepancies between the predictions of the Krumhansl-Brooks analysis and the values of their parameters calculated from the experimental data, several possibilities suggest themselves:

(1) The decomposition into z modes and xy modes may not be appropriate; one of the other decompositions which have been suggested (Komatsu and Nagamiya,[3] Klemens,[6] Gurney[5]) might be more suitable.

(2) This decomposition may be suitable, but there may be difficulties in its application: (a) The values chosen for the force constants may be incorrect. These determine ν_{1z} and ν_{1xy} and hence the transition temperatures, T_{0z} and T_{0xy}. (b) The approximation of the spectrum below ν_{1z} by the Debye parabolic form may be too crude. The region of the Brillouin zone just below ν_{1z}, where the constant-energy surfaces are not yet truncated but have their upper portions crowded together near the upper planes of the zone, would not be likely to give rise to a parabolic spectrum. The transition should depend strongly, however, on this region of the zone. (c) There may be a size effect, due to the limited number of planes (60–90) in each crystallite.[33] For waves propagating in a direction making the angle θ with the z axis, the distance in the z direction between points of equal phase is given by $\lambda_z=\lambda/\cos\theta$. If λ_z is less than the crystallite thickness, L_z, the waves may not be transmitted coherently across the crystallite boundaries.[34] Wave vectors corresponding to $\nu>\nu_{1z}$ occupy a region of the Brillouin zone for which θ cannot have arbitrarily small values and so are not affected by the above argument. Their vibration spectrum will still be linear and their contribution to C_L should still be given by Eq. (14), above T_0 as calculated by Krumhansl and Brooks. But among the waves with $\nu<\nu_{1z}$ only those with sufficiently long wavelength could be transmitted through the material without attenuation.[35] The condition for such transmission would be $\lambda_z>L_z$ and these waves would be expected to have a vibration spectrum proportional to ν^2 and thus give a T^3 contribution to C_L, since for them the material would effectively be a continuum. There would, however, be a new transition temperature $T_0'<T_0$.

A very rough quantitative check of this idea can be made by using the relation

$$(h\bar{v}/\lambda_{zm})=k\theta_D, \tag{17}$$

between $\bar{v}$, the mean velocity of sound and λ_{zm}, the minimum wavelength for such "continuum waves." If we associate λ_{zm} with $L_z\approx250$ A and take $T_0'=2$°K, relating it to θ_D by $\theta_D=5T_0'$ (since C_L is proportional to T^3 below T_0'), then $\bar{v}$ is about 5×10^5 cm/sec. This is of the same order of magnitude as for an isotropic medium with the compressibility calculated for graphite by Brennan and with Poisson's ratio about 0.3.

Of these possibilities, (1) and (2b) involve further examination of the theory, while (2a) and (2c) would seem to susceptible to experimental investigation. In order to investigate thoroughly the possibility of a size effect it would be desirable to measure the heat capacity of a single crystal. Pure single crystals large enough for low-temperature heat capacity measurements unfortunately do not seem to be available at present.

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Note added in proof.—K. Komatsu [J. Phys. Soc. Japan **10**, 346 (1955)] has recently published a new analysis of the lattice atomic heat in which he predicts a transition from T^2 to λ^3 dependence at about 2°K.

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[33] Gurney (reference 5) also discusses a size effect in connection with his model.

[34] A similar effect arising in thermal conduction in glass has been discussed by C. Kittel, Phys. Rev. **75**, 972 (1949).

[35] The same situation can also be discussed in terms of the modified Brillouin zone appropriate to crystallites of limited thickness. The general result has been described by P. P. Ewald, Proc. Phys. Soc. (London) **52**, 167 (1940).