

## Specific Heat of Various Graphites between 0.4 and 2.0°K\*

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Below 1.2°K, the specific heat of natural Madagascar graphite is:  $C = 13.8 T + 27.7 T^3 \mu\text{J/mole deg}$ . The coefficient of the linear term agrees well with theoretical calculations of the electronic specific heat of a pure single crystal of graphite. The  $T^3$  term yields a Debye parameter,  $\Theta_0$ , of 413°K. For pile graphite, lamp-black, and pyrographite it is found that the specific heat is directly dependent on the degree of stacking faults. This is in agreement with the theory which proposes that stacking faults will decrease the value of  $c_{44}$ , the elastic constant of shear between neighboring layers, which leads to additional modes at low temperatures and thus adds to the specific heat.

### INTRODUCTION

IN the past ten years, considerable work has been done regarding both the experimental and theoretical specific heat of graphite.<sup>1-11</sup> Due to the predominantly layer type structure of graphite, attempts were made to treat the lattice as a two-dimensional array, thus yielding a  $T^2$  dependence of the specific heat at low temperatures. Measurements by DeSorbo and Tyler<sup>6</sup> confirmed this  $T^2$  region for temperatures between 13 and 54°K. Later experimental<sup>7,8</sup> work down to 1°K showed that the  $T^2$  law did not hold at these lower temperatures, and a transition to  $T^3$  behavior was indicated. Komatsu<sup>2</sup> proposed that for sufficiently long phonon wavelengths at these lower temperatures, the weak shearing interaction between neighboring layers, represented by the elastic shearing constant,  $c_{44}$ , would play an important role. From his theory it follows that below 20°K the deviation from the  $T^2$  law would become apparent, and the  $T^3$  law would predominate below a few degrees Kelvin.

An extensive experimental examination by DeSorbo and Nichols<sup>9</sup> on several types of graphite specimens from 1 to 20°K, while confirming the previous work, showed in addition a significant difference between different types of graphite. The results on three different graphite samples suggested an inverse dependence of the specific heat on the crystallite size, with a temperature dependence in the region from 1.4 to 4.2°K ranging from  $T^{2.2}$  to  $T^{2.6}$ . But both Komatsu<sup>3</sup> and Bowman and Krumhansl<sup>4</sup> specifically rejected this explanation in

favor of effects arising from defect structures which also differentiated the materials. DeSorbo and Nichols evaluated these data in the usual manner of a sum of an electronic term,  $\gamma T$ , and a lattice term,  $\alpha T^3$ . By extrapolation of a plot of  $C/T$  versus  $T^2$  to 0°K, a value of  $\gamma = 25 \mu\text{J/mole deg}^2$  was found, with different  $\alpha$  values for each specimen. However, the curves did not become straight lines, even at the lowest temperatures, and the  $\gamma$  value was much larger than that predicted by theory.<sup>11</sup>

Komatsu<sup>3</sup> modified his earlier theory to encompass this particle size effect on the basis of a difference in the degree of stacking faults among neighboring layers for each of the samples. Stacking faults will reduce the value of  $c_{44}$ , thereby enabling more modes to be activated at lower temperatures, and will shift the limiting  $T^3$  behavior to lower temperatures. On the other hand, Flubacher *et al.*<sup>5</sup> proposed the existence of an additional term which extends down to 0°K, in order to explain the additional specific heat. The basis for this additional term was surface modes as predicted by Montroll.<sup>12</sup> They maintained that the  $\gamma$  value should be the theoretical value, and the  $\alpha$  values should be the same for all the samples. The additional specific heat would be of the form  $bT^2$ . The coefficient of these  $T^2$  terms would be proportional to the surface to volume ratio, and thus inversely dependent on the individual particle size. Bowman and Krumhansl<sup>4</sup> simultaneously with Komatsu concluded that stacking faults were the principle cause of the differences, having made semiquantitative calculations of the surface effects and having rejected these as insignificant in the samples measured.

By measurements down to 0.4°K, it was of interest to solve these divergent proposals with regards to the limiting low-temperature behavior of the particle size effect. Also, it was hoped that by extension down to lower temperatures a better value of  $\gamma$  could be obtained.

### EXPERIMENT

The apparatus used was the He<sup>3</sup> cryostat described previously.<sup>14</sup> Instead of a carbon resistance thermom-

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<sup>4</sup> J. C. Bowman and J. A. Krumhansl, *J. Phys. Chem. Solids* **6**, 367 (1958); see also J. A. Krumhansl and H. Brooks, *J. Chem. Phys.* **21**, 1663 (1953).

<sup>5</sup> P. Flubacher, A. J. Leadbetter, and J. A. Morrison, *J. Phys. Chem. Solids* **13**, 160 (1960).

<sup>6</sup> W. DeSorbo and W. W. Tyler, *J. Chem. Phys.* **21**, 1660 (1953).

<sup>7</sup> U. Bergenlid, R. W. Hill, F. J. Webb, and J. Wilks, *Phil. Mag.* **45**, 851 (1954).

<sup>8</sup> P. H. Keesom and N. Pearlman, *Phys. Rev.* **99**, 1119 (1955).

<sup>9</sup> W. DeSorbo and G. E. Nichols, *J. Phys. Chem. Solids* **6**, 352 (1958).

<sup>10</sup> P. R. Wallace, *Phys. Rev.* **71**, 622 (1947).

<sup>11</sup> J. W. McClure, *Phys. Rev.* **108**, 612 (1957).

<sup>12</sup> E. W. Montroll, *J. Chem. Phys.* **18**, 183 (1950).

<sup>13</sup> C. A. Klein, *Rev. Mod. Phys.* **34**, 56 (1962).

<sup>14</sup> G. M. Seidel and P. H. Keesom, *Rev. Sci. Instr.* **29**, 606 (1958).

eter, a highly doped ( $6 \times 10^{17} \text{ cm}^{-3}$  antimony), highly compensated ( $5 \times 10^{17} \text{ cm}^{-3}$  gallium) germanium resistance thermometer was glued to the top of the sample with glyptal lacquer. Resistance range for a typical measurement was  $15\Omega$  at  $4.2^\circ\text{K}$ ,  $50\Omega$  at  $1.0^\circ\text{K}$ , and  $200\Omega$  at  $0.4^\circ\text{K}$ . Dimensions of the thermometer were 3 mm by 1 mm by 1 mm, and the weight was 0.036 g. Copper leads were soft soldered (50% lead-50% tin) to the ends. Correction for the heat capacity of the addenda (germanium, copper, constantan heater wire, solder, and glyptal lacquer) amounted to less than 2% of the heat capacity of the sample at the lowest temperature. The specific heat of germanium in this temperature range is much smaller and more accurately known than that of the carbon resistor formerly used. Calibration of the thermometer was done using the 1962-He<sup>3</sup> temperature scale of Sydoriak and Roberts<sup>15</sup> for the range 0.4 to  $1.2^\circ\text{K}$ , in conjunction with a paramagnetic salt thermometer for values below  $0.5^\circ\text{K}$ , and

TABLE I. Specific heat of the various graphites. (C is in  $\mu\text{J}/\text{mole deg.}$ )

$T, ^\circ\text{K}$	$C$	$T, ^\circ\text{K}$	$C$
NMG		Pyrographite	
0.3816	6.85	0.4546	24.50
0.4090	7.59	0.4918	29.18
0.4275	8.17	0.5287	33.97
0.4613	9.07	0.5981	44.13
0.4250	7.98	0.6479	53.75
0.4475	8.56	0.7298	68.86
0.5011	10.41	0.8237	91.31
0.5404	11.80	0.9116	115.55
0.5905	13.70	0.9766	134.02
0.6352	15.69	1.0578	158.59
0.6686	17.59	1.1500	191.49
0.7214	20.42	1.2467	229.34
0.7571	22.37	1.3786	289.90
0.8089	25.89	1.5620	389.51
0.8419	28.19	1.7717	514.31
0.8879	31.81	2.0134	680.34
0.9429	36.17		
1.0095	42.39		
1.0899	50.76		
1.1563	58.14		
1.2507	68.87		
1.3516	84.37		
1.4644	102.37		
1.6637	139.04		
1.8722	182.37		
Pile graphite		Lampblack	
0.4477	13.77	0.3747	18.33
0.4829	15.54	0.4401	24.45
0.5821	21.04	0.5217	33.84
0.7175	30.23	0.6194	47.34
0.8025	37.74	0.7252	65.92
0.9120	49.37	0.8185	84.87
0.9469	53.55	1.0138	135.43
1.1066	74.50	1.1425	175.08
1.2689	100.32	1.4414	289.82
1.4906	148.05	1.5445	336.19
1.7729	222.17	1.7809	459.72
1.9532	282.34	1.9151	541.94
2.1395	353.82	2.0068	598.17

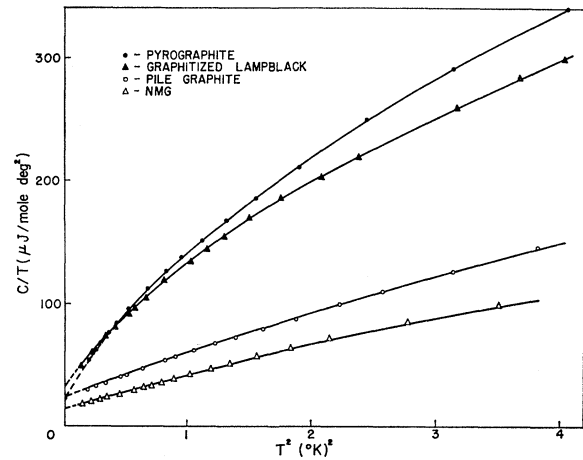


FIG. 1. Specific heat of the various graphites plotted as  $C/T$  vs  $T^2$ .

the 1958-He<sup>4</sup> temperature scale<sup>16</sup> above  $1.0^\circ\text{K}$ . A fit of  $(\log R/T)^{1/2}$  versus  $\log R$  by the method of least squares was done on an IBM 7090 digital computer.

In order to eliminate spurious heating of the thermometer due to extraneous electrical impulses,  $C-L-C$  filters were built into all input and output leads at the top of the cryostat. These blocked all frequencies above 2000 cps. In addition, the dewars were shielded with copper screen. The method proved very successful.

To eliminate the effect of absorbed gases on the graphite specimens, the samples were pumped for at least three days at room temperature. The total experimental error is estimated to be not greater than  $\pm 2\%$ .

Four different graphite specimens were measured in the temperature range from 0.4 to  $2.0^\circ\text{K}$ :

- I. Natural Madagascar graphite (NMG)-5.09 moles, average crystallite dimension  $> 100 \mu$ , very low degree of stacking faults.
- II. Pile graphite-6.38 moles, average crystallite dimension  $L = 240 \text{ \AA}$ , low degree of stacking faults.
- III. Graphitized lampblack (SA25)-3.44 moles, average crystallite dimensions  $L_c = 125 \text{ \AA}$ ,  $L_a = 90 \text{ \AA}$ , high degree of stacking faults.
- IV. Pyrographite-2.14 moles, average crystallite dimensions  $L_c = 265 \text{ \AA}$ ,  $L_a = 200 \text{ \AA}$ , very high degree of stacking faults.

RESULTS

The results of the measurements in the region from 0.4 to  $2.0^\circ\text{K}$  are presented in Table I. These are also graphically represented in Fig. 1 in the form  $C/T$  versus  $T^2$ . If  $C$  is the total specific heat, then the formula,

$$C = \gamma T + \alpha T^3,$$

should give a straight line with intercept  $\gamma$  and slope  $\alpha$ . Here  $\gamma T$  represents the electronic contribution to the

<sup>15</sup> S. G. Sydoriak, T. R. Roberts, and R. H. Sherman, in Eighth International Congress on Low Temperature Physics, London, 1962 (unpublished), p. 297.

<sup>16</sup> F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. **64A**, 1 (1960).

specific heat, and  $\alpha T^3$  the contribution due to a three-dimensional lattice. For the case of NMG and pile graphite, this way of representing the data is correct below 1.0°K. Above 1.0°K both curves begin to deviate gently from the straight line, indicating a transition to the  $T^2$  region. For the case of pyrographite and graphitized lampblack it appears that this transition to a  $T^2$  behavior begins at much lower temperatures.

For NMG the slope  $\alpha$  is equal to 27.7  $\mu\text{J}/\text{mole deg}^4$ , which yields a value for the Debye parameter,  $\Theta_0$ , of 413°K. The same sample gives a value for  $\gamma$  of 13.8  $\mu\text{J}/\text{mole deg}^2$ . These values are expected to be characteristic for a pure single crystal of graphite.

For pile graphite the  $\gamma$  value is 23.3  $\mu\text{J}/\text{mole deg}^2$ . In the case of pyrographite and graphitized lampblack, much greater uncertainty in the extrapolation exists, but values of  $\gamma$  equal to 20 and 30  $\mu\text{J}/\text{mole deg}^2$ , respectively, are found.

## DISCUSSION

### Lattice Specific Heat

The ideal graphite lattice is made up of carbon atoms arranged in layers according to a two-dimensional hexagonal pattern. The layers are stacked on top of one another in an *abab* scheme, such that every other layer is located directly above the first. The distance between neighboring atoms in the same layer is,  $a=1.42 \text{ \AA}$ , and between adjacent layers,  $c=3.35 \text{ \AA}$ .

In actual practice, however, this basic graphite structure may be significantly modified, depending on the nature of the formation of the graphite. NMG follows most closely to the pattern described above, being composed of naturally formed large single crystals ( $>100 \mu$ ). The artificially formed graphites, pile graphite, lampblack, and pyrographite, all deviate from this pattern. These deviations, observed by x-ray analysis, may be characterized in two ways: (1) the single crystallite size, and (2) the degree to which the adjacent hexagonal layers are rotated and shifted with respect to one another, and their interlayer distance increased. This latter effect is referred to as the stacking faults.

The theory of the lattice vibrations of pure monocrystalline graphite has been thoroughly investigated.<sup>1-4</sup> Three kinds of modes are postulated: (1) transverse in-plane vibrations, (2) longitudinal in-plane vibrations, and (3) out-of-plane or bending vibrations. (1) and (2) are independent vibrations. The out-of-plane modes contain terms dependent on the shearing interactions ( $c_{44}$ ), and are also dependent upon (2). If one examines the constant frequency contours with respect to the first Brillouin zone, the following picture is obtained. For modes (1) and (2) these constant frequency contours form prolate (cigar-shaped) ellipsoids with the major axis along the  $\sigma_c$  direction. In the reciprocal lattice the  $\sigma_c$  axis lies along the  $z$  axis, perpendicular to the planes, and the  $\sigma_a$  axis in the  $xy$  plane. At a frequency  $\nu_z$ , corresponding to a temperature of 20°K, these ellipsoids be-

come truncated by intersection with the boundary of the first Brillouin zone at  $\sigma_c=\pm 1/2c$ . From the proposed frequency spectrum in these two regions [ $f(\nu)\propto\nu^2$  for  $\nu<\nu_z$ ,  $f(\nu)\propto\nu$  for  $\nu>\nu_z$ ], one expects modes (1) and (2) to yield  $T^3$  behavior below 20°K and a  $T^2$  behavior above. By far the largest contribution to the specific heat at the lowest temperature arises from the modes (3). For these modes, the constant frequency contours are prolate (disc shaped) ellipsoids with the major axis along the  $\sigma_a$  direction. It is found that at a frequency  $\nu_z'\propto c_{44}$ , corresponding to a temperature of 2°K, a  $T^3$  to  $T^2$  transition occurs for this model. This transition is not due to truncation by the first Brillouin zone at  $\sigma_a=\pm 1/2a$ , but is a consequence of the more involved nature of the frequency dependence of this (3) mode term.

The over-all picture one expects, therefore, is a pure  $T^3$  region below 2°K, a transition region of a large  $T^2$  term and a small  $T^3$  term between 2 and 20°K, and a  $T^2$  region above 20°K. Evidently this approach is consistent with our data and the data of DeSorbo and Nichols<sup>9</sup> on Canadian natural graphite extended to 20°K.

Accepting this theory as a basis for the specific heat of a large single crystal structure, unmarred with the presence of stacking faults, one may now examine the source of this type dependence. There are two divergent theories. Komatsu,<sup>3</sup> as well as Bowman and Krumhansl,<sup>4</sup> proposed that the increase of stacking faults is accompanied by a reduction of  $c_{44}$ . This implies an additional elongation of the (3) mode ellipsoids along the major axes (but not a reduction of the minor axis), such that the frequency,  $\nu_z'$ , is reduced, and thus the transition temperature lowered. Also the relative magnitude of this term would increase due to the larger volume of the ellipsoid available at a given frequency. Hence, more low frequency modes would be excited at a given temperature in this more loosely bound lattice. The net effect in the lowest temperature range ( $T<1.0^\circ\text{K}$ ) is a larger specific heat with increasing degree of stacking faults. This agrees with the observations.

As mentioned in the introduction, Flubacher *et al.*<sup>5</sup> proposed that the magnitude of the specific heat was not dependent on the stacking faults. Instead they felt that, due to surface modes, the additional specific heat of the synthetic graphites would be inversely related to the particle size.

If this size effect were indeed the cause of the additional contribution, one would expect the specific heat of pyrographite and pile graphite to be of the same magnitude, both having a particle size of approximately 250  $\text{\AA}$ . In disagreement with this prediction, pyrographite, the sample with the highest degree of stacking faults, had the highest specific heat. Furthermore, none of the samples displayed a  $T^2$  behavior all the way down to absolute zero. It is felt that this size effect will not persist at low temperatures.

If one makes a rough approximation of the phonon wavelength, using the relation  $\lambda = hc/kT$ , and letting  $c = 10^6$  cm/sec, a value calculated by Komatsu from the elastic constants, it is found that the phonon wavelength is much larger than the average particle size. Consequently, the surface modes should play a negligible role in any specific heat contribution within this temperature range.

Annealing for three hours at 2500°C should remove most of the stacking faults.<sup>13</sup> This would result in a reduction of the specific heat by 50%, a value similar to that of pile graphite. Due to difficulties with the induction furnace, an anneal of only one hour was achieved. Nonetheless, a reduction of 15% was observed. It is expected that annealing will also increase the crystallite size. However, the crystallite size of pyrographite is already relatively large, and such an anneal should not increase the crystallite size by an amount at all sufficient to account for this decrease in specific heat. It follows that the reduction was due primarily to the decrease in degree of stacking faults.

It is concluded, therefore, that the theories of Komatsu and of Bowman and Krumhansl agree very well with the experimental results, and that the theory of Flubacher *et al.* is in disagreement with these results.

#### Electronic Specific Heat

A great deal of attention has been given to the band structure of pure graphite.<sup>10,11</sup> It was found that a small interaction between second nearest planes in the *abab* structure gives rise to a small overlap of the valence and

conduction bands at the Fermi level. Thus, the density of states at the Fermi level has a small, yet distinguishable value. This yielded a value of  $\gamma$ , the coefficient of the linear electronic term in the specific heat of 12.6  $\mu\text{J}/\text{mole deg}^2$ . The measurements on NMG give a value of  $\gamma = 13.8 \mu\text{J}/\text{mole deg}^2$ . This is in good agreement with the theoretical value.

For the other samples, slightly higher values for  $\gamma$  were obtained. Any acceptor or donor states due to physical defects or chemical impurities will shift the Fermi level into regions of higher density of states. The density of states curve is sufficiently steep where the bands overlap so that a small shift in the Fermi level results in a large change in the density of states at the Fermi level. Stacking faults, on the other hand, will decrease the interaction between second nearest planes, and thus reduce the amount of band overlap.

As a result, additional states can account for the larger  $\gamma$  values of the synthetic graphites. The very high degree of stacking faults in pyrographite may well explain its lower  $\gamma$  value, a value lower than that of either lampblack or pile graphite.

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