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## Anisotropic Thermal Expansion of Pyrolytic Graphite at Low Temperatures

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# Anisotropic Thermal Expansion of Pyrolytic Graphite at Low Temperatures

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Interferometric measurements of the linear thermal-expansion coefficients  $\alpha_{||}$  and  $\alpha_{\perp}$  in the "c" and "a" axial directions of well-oriented pyrolytic graphite between approximately 20° and 270°K are reported. Grüneisen parameters  $\gamma_{||}$  and  $\gamma_{\perp}$ , defined for strain coordinates parallel and perpendicular to the "c" axis, respectively, have been calculated from the present thermal expansion coefficients and related data. Between 30° and 270°K  $\gamma_{||}$  is positive, indicating the preponderance of longitudinal modes of vibration, while  $\gamma_{\perp}$  is negative, indicating the predominance of transverse modes. The quasi-harmonic approximation has been applied to calculate the characteristic temperatures  $\theta(n)$  corresponding to the maximum frequencies  $\omega_D(n)$  of the Debye distributions having the same  $n$ th moments  $\langle \omega^n \rangle$  as the specimens, which vary between approximately 420° and 2270°K as  $n$  increases from  $-3$  to  $+6$ . The dimensional dependence of the moments, defined by  $\gamma(n) = \Sigma \gamma_j \omega_j^n / \Sigma \omega_j^n$  corresponding to  $\gamma_{||}(n)$  and  $\gamma_{\perp}(n)$ , and their variations with  $n$ , are consistent with the existence of low-frequency modes of vibration between planes of atoms perpendicular to the "c" axis, and high-frequency modes within the planes, a result supported by calculations of the rms displacements of the atoms.

## INTRODUCTION

Studies of the lattice dynamics of pyrolytic graphite have figured prominently in recent years, among which may be mentioned calculations of the optical and acoustic modes of vibration,<sup>1</sup> applications of a semicontinuum model,<sup>2,3</sup> and considerations of particle size and stacking faults.<sup>4,5</sup> Calculations have been extended to atomic amplitudes of vibration<sup>6,7</sup> to thermal-expansion coefficients<sup>8</sup> and to calculations of the frequency spectrum on the basis of Born-von Kármán theory.<sup>9</sup> An intrinsic interest in the thermal expansion of graphite exists because of its hexagonal structure, however, and a convenient approach to a study of its thermal-expansion characteristics may be made via the Grüneisen parameter.

Arising largely from the recent works of Kelly,<sup>6-8</sup> and associated with disagreements between existing measurements of thermal-expansion coefficients at 0°C amounting to approximately 20% for values in the "c" direction and 40% in the "a" direction, measurements of the thermal-expansion coefficients of well-oriented pyrolytic graphite have been undertaken in the temperature range 20°–273°K.

## EXPERIMENTAL DETAILS AND RESULTS

The Fizeau interferometric apparatus which was used for the measurements has been described earlier.<sup>10</sup> Specimens loaned from the UKAEA Reactor Materials Laboratory, Culcheth, were fashioned to the shape of small blocks, approximately  $5 \times 10^{-3}$ -m cube, by cleaving and rubbing. The same three specimens were used for measurements in the "c" and "a" directions, after being aligned to within 0.25° by means of back-reflection Laue photographs. Smoothed results of the measurements are summarized in Table I. Typical uncertainties in the linear-expansion coefficients  $\alpha_{||}$  in the "c" direction are believed to rise from 3% at 250°K through 4% at 100°K to 6% at 50°K. For the measurements  $\alpha_{\perp}$

in the "a" direction corresponding figures are 6% at 250°K through 6% at 150°K, 8% at 100°K and 12% at 50°K to 20% at 30°K.

## THE GRÜNEISEN PARAMETERS

In accordance with recent extensions of representations of the Grüneisen parameter to axial crystals,<sup>11</sup> the Grüneisen parameters  $\gamma_{||}$  and  $\gamma_{\perp}$  for a solid having hexagonal symmetry are given by

$$\gamma_{||} = (V/C_t)(2c_{13}^s \alpha_{\perp} + c_{33}^s \alpha_{||})$$

and

$$\gamma_{\perp} = (V/C_t)[(c_{11}^s + c_{12}^s)\alpha_{\perp} + c_{13}^s \alpha_{||}]$$

in which  $c_{ij}^s$  are adiabatic elastic constants,  $C_t$  is the heat capacity of volume  $V$  at constant stress and the symbols  $||$  and  $\perp$  denote directions parallel and perpendicular to the "c" axis, respectively. The only comprehensive sets of data currently available for these appear to be those of Reynolds<sup>12</sup> and Soule and Nezbeda.<sup>13</sup> Assuming 97.5% of the theoretical density given by Taylor,<sup>14</sup>  $V_{270}$  was taken as  $5.459 \times 10^{-6}$  m<sup>3</sup> g atom<sup>-1</sup>. The present thermal-expansion results were then used in association with the specific-heat results of De Sorbo and Tyler<sup>15</sup> and Jacobs and Parks<sup>16</sup> to calculate  $\gamma_{||}$  and  $\gamma_{\perp}$  as functions of temperature producing the results displayed graphically in Fig. 1. No allowance was made in these calculations for the temperature variations of the  $c_{ij}^s$ , which are unknown at the present time. Excluding any such influence, the absolute uncertainties in these values increase from approximately 4% at 270°K to approximately 9% at 40°K in the case of  $\gamma_{||}$ , and from approximately 7% at 270°K to approximately 23% at 40°K in the case of  $\gamma_{\perp}$ . Extrapolations of the  $\gamma_{\lambda}$  vs  $T$  plots to temperature-independent regions yielded values of  $\gamma_{||}(-3) = 3.5 \pm 1.5$  and  $\gamma_{\perp}(-3) = -(5.5 \pm 1.5)$ , in which the error limits are estimated. In this notation  $\gamma_{\lambda}(-3)$  are the low-temperature limiting values of  $\gamma_{\lambda}$ .

TABLE I. Smoothed thermodynamic data for pyrolytic graphite.

$T$ (°K)	$\alpha_{  }$ ( $\times 10^5$ deg $^{-1}$ K)	$-\alpha_{\perp}$ ( $\times 10^5$ deg $^{-1}$ K)	$C_i - C_n$ (J/g atom deg)
30	0.38	(0.09)	(0.000)
40	0.60	0.32	0.000
50	0.87	0.50	0.001
60	1.13	0.66	0.002
80	1.49	0.89	0.003
100	1.76	1.07	0.006
120	1.98	1.19	0.009
140	2.15	1.28	0.013
160	2.29	1.32	0.017
180	2.41	1.34	0.021
200	2.50	1.33	0.025
220	2.58	1.32	0.029
240	2.65	1.31	0.033
260	2.69	1.28	0.037
270	(2.72)	(1.27)	(0.039)

### THE HEAT CAPACITY

Before proceeding with an application of the quasi-harmonic approximation to calculations of the moments of the vibrational frequency distribution of graphite, and their volume dependence, it was necessary to calculate  $C_n$ , the specific heat at constant strain, from the experimental  $C_i$  data. The calculated values of  $C_i - C_n$  are summarized in Table I, which are believed to be correct within approximately 11% at 270°K.

The electronic-heat coefficient of natural Madagascar graphite given by Komatsu<sup>5</sup> was used to calculate the electronic contribution to the heat capacity, as  $1.36 \times 10^{-5} T$  J/deg g atom, and hence to correct the calculated values of  $C_n$  to give the lattice contribution  $C_n^l$ , before proceeding to the calculation of the moments of the frequency distribution described later. Typically the electronic contribution amounts to 0.05% of the lattice contribution at 270°K, rising to 0.4% at 20°K.

### THE MOMENTS OF THE FREQUENCY DISTRIBUTION

The importance of the moments  $\langle \omega^n \rangle$  of the frequency distribution  $G(\omega)$  given by

$$\langle \omega^n \rangle = \left( \int_0^\infty \omega^n G(\omega) d\omega \right) / \left( \int_0^\infty G(\omega) d\omega \right)$$

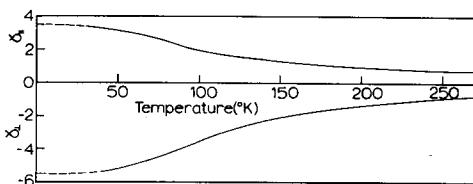


FIG. 1. The Grüneisen parameters  $\gamma_{||}$  and  $\gamma_{\perp}$  of pyrolytic graphite, corresponding to the "c" and "a" crystallographic axis directions, respectively, as functions of temperature.

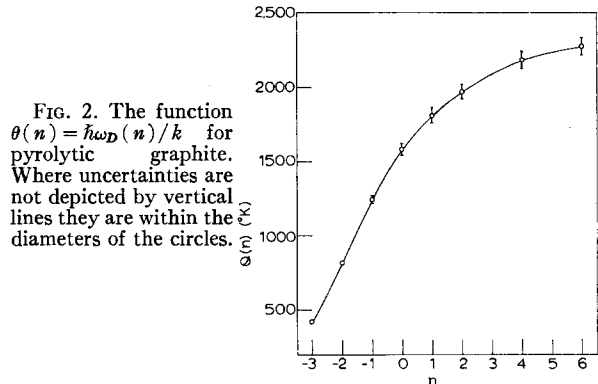


FIG. 2. The function  $\theta(n) = \hbar\omega_D(n)/k$  for pyrolytic graphite. Where uncertainties are not depicted by vertical lines they are within the diameters of the circles.

and the maximum frequencies  $\omega_D(n)$  of the Debye distributions having the same  $n$ th moments as the actual crystal,

$$\omega_D(n) = [(n+3) \langle \omega^n \rangle / 3]^{1/n} \quad (n \neq 0, n > -3)$$

are well known. Applications of the quasi-harmonic approximation, in which account is taken of purely volume-dependent effects upon the vibrational characteristics, have been applied to the calculation of moments of the vibrational frequency spectra of alkali halides.<sup>17,18</sup> Explicitly temperature-dependent effects are unlikely to make a significant contribution to the free energy below temperatures of approximately  $\theta_\infty/3$ , and the procedure outlined by the former workers has been applied to the analysis of the present experimental data. In this analysis the heat-capacity data of Magnus<sup>19</sup> were used above room temperature, and  $\theta^c(0, \eta_0)$  was taken as  $420 \pm 10^\circ\text{K}$ .<sup>20</sup> Adopting the representation  $\theta(n) = \hbar\omega_D(n)/k$  the moments are displayed in Fig. 2. If these results are compared with corresponding results available for simple solids, two

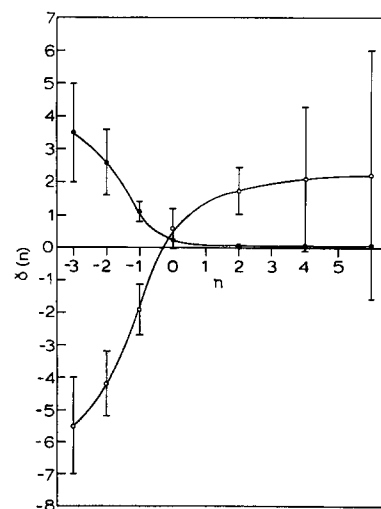


FIG. 3. The variation of  $\gamma_\lambda(n)$  with  $n$  for pyrolytic graphite, in which the uncertainties are indicated by the vertical lines: ●  $\gamma_{||}(n)$ , corresponding to the "c" crystallographic axis direction. ○  $\gamma_{\perp}(n)$ , corresponding to the "a" crystallographic axis direction.

TABLE II. Vibrational amplitudes in pyrolytic graphite.

$T$ (°K)	rms amplitude ( $\times 10^{11}$ m)
0	0.49
1000	1.36
2000	1.91
3000	2.33
4000	2.69

distinguishing features stand out immediately in the variation of  $\omega_D(n)$  with  $n$ : (i) the spread in values among the  $\omega_D(n)$  in the range  $-3 \leq n \leq 6$  is considerably greater in the case of graphite, and (ii) no minimum in  $\omega_D(n)$  occurs within this range of  $n$ . From these observations it is clear that the actual vibrational frequency spectrum of graphite must be particularly complex.

### THE VOLUME DEPENDENCE OF THE MOMENTS

The influence of volume upon the characteristic temperatures corresponding to the entropy, heat capacity and the Debye-Waller frequency integral may all be calculated with the aid of the volume dependence of the moments,<sup>21</sup> conveniently expressed in terms of the parameter:

$$\begin{aligned}\gamma(n) &= \sum_{j=1}^{3N-6} \gamma_j \omega_j^n / \sum_{j=1}^{3N-6} \omega_j^n \\ &= -d \ln \omega_D(n) / d \ln V \\ &= -(1/n) (d \ln \langle \omega^n \rangle / d \ln V)\end{aligned}$$

for an assembly of  $N$  atoms.

The methods adopted to determine values of  $\gamma(n)$  for  $-3 \leq n \leq 6$  have been summarized earlier,<sup>21,22</sup> and the results of the calculations are displayed graphically in Fig. 3.

The fact that  $\gamma_{11}(6) \doteq 0$  implies that  $\langle \omega^n \rangle$  is sensibly independent of small dimensional changes for  $n=2, 4, 6$ . These moments are determined largely by the higher frequencies of the spectrum, and relatively loose coupling between the layers of atoms lying perpendicular to the “ $c$ ” axis may be inferred. On the other hand  $\gamma_{11}(-3)$  is very much larger and positive, implying a much greater sensitivity to dimensional changes of the low-frequency modes, in which the major contribution is longitudinal, and which determine its magnitude. By analogy with a simple vibrating system, this observation too is consistent with weak forces between the planes perpendicular to the “ $c$ ” axis, and the rapid fall of  $\gamma_{11}(n)$  with  $n$  increasing from  $-3$  suggests that the interplanar forces must be particularly weak, a fact which is consistent with the mechanical properties of graphite.  $\gamma_{11}(6)$  is large, however, implying a large dimensional dependence of the high-frequency modes within the planes perpendicular to the “ $c$ ” axis.

### THE VIBRATIONAL AMPLITUDES

Starting with a result deduced by Blackman<sup>23</sup> on the basis of assumed harmonic lattice vibrations, Leadbetter<sup>24</sup> has used the Debye-Waller frequency integral  $X(T)$  discussed by Barron *et al.*<sup>25</sup> to derive expressions for the mean-square amplitudes of the atoms and molecules of ice. Adapting these expressions to the present situation, the mass  $m$  and the mean-square amplitude of vibration of the carbon atoms  $\langle u^2 \rangle$  are related to  $X(T)$  through  $m \langle u^2 \rangle = X(T)$ . In the low-temperature limit  $X(T) = \hbar \langle \omega^{-1} \rangle / 2$ , while for  $T > \theta / 2\pi$ ,

$$\begin{aligned}X(T) &= kT [\langle \omega^{-2} \rangle + (1/12) (\hbar/kT)^2 \\ &\quad - (1/720) (\hbar/kT)^4 \langle \omega^2 \rangle \cdots].\end{aligned}$$

Root-mean-square amplitudes calculated from these equations are listed in Table II. Kelly<sup>6</sup> has calculated the thermal vibrational amplitudes of carbon atoms in the graphite lattice parallel to the “ $c$ ” axis, on the basis of a semicontinuum model.<sup>2,3</sup> Comparing the results of his calculations with available x-ray data, Kelly concluded that the elastic constant  $c_{44}$  was between  $2.26 \times 10^9$  and  $2.26 \times 10^{10}$  N/m<sup>2</sup>, a conclusion which proved to be consistent with the subsequent measurement of Soule, reported by Reynolds,<sup>12</sup>  $c_{44} = 3.9 \times 10^9$  N/m<sup>2</sup>. The results of the present calculations will be seen to lie below the mean of Kelly's results corresponding to  $c_{44}$  equal to  $2.26 \times 10^9$  and  $2.26 \times 10^{10}$  N/m<sup>2</sup> by approximately 25% over most of the temperature range 0°–4000°K, except at the lowest temperatures, where the agreement is excellent. This is in accordance with expectation. At the lowest temperatures only the low-frequency modes will be excited, which are likely to consist mostly of the vibrations associated with the relatively weak bonds between the planes which lie perpendicular to the “ $c$ ” axis. These are the “out-of-plane” modes considered by Kelly. At higher temperatures, however, the higher frequency “in-plane” modes will be excited, the amplitudes of which would be expected to be lower than those of the “out-of-plane” modes. The root-mean-square amplitude given by the present quasiharmonic analysis refers to all the vibrations in the solid, and would therefore be expected to be somewhat lower than the root-mean-square amplitude of the “out-of-plane” modes taken separately.

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## Thermal Expansion of Molecular Crystals and Its Graphical Display

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## Role of Thermal-Expansion Measurements in the Experimental Graphite Program

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## Lattice Dynamics of Argon at 4°, 40°, and 77°K

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Neutron scattering techniques have been used to measure phonon dispersion relations in a 1-ml single crystal of <sup>36</sup>Ar. Data were taken along the 100 crystallographic direction for the transverse mode at 4°, 40°, and 77°K. The measurements were performed on a free-standing crystal in equilibrium with its own vapor pressure. Preliminary analysis of the results yields mean shifts of the frequency of the transverse mode of 7% at 40°K and 21% at 77°K, relative to the 4°K value. These frequency shifts appear to decrease slightly with increasing wave vector. The mean Grüneisen parameter for this mode between 4° and 77°K is then  $3.2 \pm 0.4$  if it is assumed that the frequency shifts are due to the change in volume alone. Good agreement is found between the experimental frequency shifts and those predicted using a classical lattice dynamical model.<sup>1</sup>

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