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THE THERMAL EXPANSION COEFFICIENT OF GRAPHITE PARALLEL TO THE BASAL PLANES

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Abstract—The theory of thermal expansion of a graphite crystal is applied parallel to the basal planes. It is shown that the observed expansion at high temperatures is less than expected. A calculation is made of the effect on thermal expansion of an unusual anharmonicity for the out-of-plane bond bending vibrations. The consequences of this model are discussed with regard to the very low temperature behaviour of the basal expansion coefficient.

INTRODUCTION

Two theories of the thermal expansion coefficient of a graphite crystal have been proposed. The first theory due to D. P. Riley[1], based on the work of Gruneisen and Goens[2], assumed Debye[3]—type dispersion relations with two distinct characteristic temperatures θ_z and θ_{xy} for vibrations polarised perpendicular ('out-of-plane') and parallel (in-plane) to the layers respectively. The negative expansion coefficient observed below 400°C in this theory is due to the Poisson contraction of the layer planes associated with the large expansion perpendicular to the layer planes. At temperatures above 400°C this effect was assumed to be counteracted by a true thermal expansion of the layer planes to produce a small positive thermal expansion coefficient.

The second theory due to Kelly and Walker[4] was based on the lattice dynamics of graphite due to Komatsu[5] and provides a good fit to the thermal expansion coefficient data perpendicular to the basal planes. It was not found possible to fit the data parallel to the basal planes because no independent estimate was available of the anharmonic coefficients.

In both theories the negative component of the basal expansion coefficient can only be explained by Poisson's ratio effect if the elastic compliance ratios is $S_{13}/S_{33} = -0{\cdot}07$ whereas recent data gives a value of $-0{\cdot}012$ [6]. It is necessary to find another component of negative expansion to explain the results. Two possible explanations are available:

(1) One of the anharmonic coefficients associated with the out-of-plane acoustic mode has the opposite sign to that expected.

(2) There is a significant negative component due to some other mechanism—some possibilities have been described by Barron[7].

In this work the theory of expansion coefficients due to Kelly and Walker[4] is extended to high temperatures using the first of these assumptions and it is shown that this is a possible mechanism. If the mechanism is correct it is possible to come to some conclusions about the thermal expansion coefficient at very low temperatures. A preliminary discussion of the second possibility is given.

THEORY

The basal expansion coefficient of a graphite crystal α_a is the sum of contributions from the 'in-plane' and 'out-of-plane' acoustic modes and optical modes. In previous studies of the properties of graphite crystals it has been shown that a two dimensional model is very satisfactory at high temperatures, that is the interaction between layers is set equal to zero. In terms of the usual elastic constants:

$$C_{13} = C_{33} = C_{44} = 0 \qquad (1)$$

In these conditions the equations given by Kelly and Walker[4] for the acoustic mode contribution to the thermal expansion coefficient parallel to the basal planes can be integrated directly:

(a) *In-plane 'longitudinal' modes*

$$\alpha_1(T) = -\frac{\pi(S_{11}+S_{12})C_{11}k}{\rho d {V_L}^4}\left[\frac{kT}{h}\right]^2\left\{\frac{1}{C_{11}}\cdot\frac{\partial C_{11}}{\partial e_{xx}}\right\}$$

$$\times J_3(\theta_L/T)$$

$$= -\frac{\pi k {\sigma_m}^2}{\rho d {V_L}^4}\left[\frac{T}{\theta_L}\right]^2\left\{\frac{1}{C_{11}}\cdot\frac{\partial C_{11}}{\partial e_{xx}}\right\}J_3(\theta_L/T) \qquad (2)$$

(b) *In-plane 'transverse' modes*

$$\alpha_2(T) = -\frac{\pi(S_{11}+S_{12})}{\rho d {V_T}^4}\frac{1}{2}(C_{11}-C_{12})k\left[\frac{kT}{h}\right]^2$$

$$\times\left\{\frac{1}{\frac{1}{2}(C_{11}-C_{12})}\cdot\frac{\partial}{\partial e_{xx}}\frac{1}{2}(C_{11}-C_{12})\right\}$$

$$\times J_3(\Theta_T/T)$$

$$\cdot = \cdot -\frac{0{\cdot}36\pi k {\sigma_m}^2}{\rho d {V_T}^4}\left[\frac{T}{\theta_T}\right]^2\left\{\frac{1}{\frac{1}{2}(C_{11}-C_{12})}\right.$$

$$\left.\cdot\frac{\partial}{\partial e_{xx}}\frac{1}{2}(C_{11}-C_{12})\right\}J_3(\theta_T/T) \qquad (3)$$

(c) *'Out-of-plane' modes*

$$\alpha_3(T) = -\frac{1}{2}\frac{k}{d\delta}(S_{11}+S_{12})\left[\frac{kT}{h}\right]\left\{\frac{1}{\delta}\cdot\frac{\partial\delta}{\partial e_{xx}}\right\}$$

$$\times J_2(\theta_0/T)$$

$$= -\frac{k}{d}(S_{11}+S_{12})\pi{\sigma_m}^2\left[\frac{T}{\theta_0}\right]\left\{\frac{1}{\delta}\cdot\frac{\partial\delta}{\partial e_{xx}}\right\}$$

$$\times J_2(\theta_0/T) \qquad (4)$$

where

e_{xx}	is the strain parallel to the layer planes
k	is Boltzmann's constant
h	is Planck's constant
σ_m	is the equivalent radius of the first Brillouin zone[4]
S_{IJ} and C_{IJ}	are the usual elastic compliances and constants
δ	is the bond bending constant
θ_L, θ_T and θ_0	are characteristic temperatures
V_L and V_T	are the longitudinal and transverse wave velocities in the layer plane
d	is the interlayer spacing

The numerical values are given in Table 1.

Table 1. Values of parameters used in calculations

Parameter	Numerical values
S_{11}	$0{\cdot}98 \times 10^{-13}$ cm^2 dyne^{-1}
S_{12}	$-0{\cdot}16 \times 10^{-13}$ cm^2 dyne^{-1}
S_{13}	$-0{\cdot}33 \times 10^{-13}$ cm^2 dyne^{-1}
S_{33}	$27{\cdot}4 \times 10^{-13}$ cm^2 dyne^{-1}
S_{44}	$0{\cdot}25 \times 10^{-10}$ cm^2 dyne^{-1}
C_{11}	$1{\cdot}06 \times 10^{13}$ dynes cm^{-2}
C_{12}	$0{\cdot}18 \times 10^{13}$ dynes cm^{-2}
C_{13}	$0{\cdot}015 \times 10^{13}$ dynes cm^{-2}
C_{33}	$3{\cdot}65 \times 10^{11}$ dynes cm^{-2}
C_{44}	$4{\cdot}0 \times 10^{10}$ dynes cm^{-2}
δ	$6{\cdot}11 \times 10^{-3}$ cm^2 sec^{-1}
V_L	$2{\cdot}01 \times 10^6$ cm sec^{-1}
V_T	$1{\cdot}23 \times 10^6$ cm sec^{-1}
δ_m	$2{\cdot}46 \times 10^7$ cm^{-1}
d	$3{\cdot}353 \times 10^{-8}$ cm
ρ	$2{\cdot}26$ g cm^{-3}
θ_L	2350°K
θ_T	1500°K
θ_0	1120°K

The $J_n(x)$ are Debye integrals of order n, and are tabulated[8].

We are interested in the expansion coefficient over a wide range of temperatures and thus we cannot neglect possible optical mode contributions. Examination of the results of Yoshimori and Kitano[9] indicates that the 'out-of-plane' optical mode contribution is parallel to the layer

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essentially two dimensional in character and it can be included by simply extending the Brillouin zone to include the additional vibrational modes. Including the optical mode contribution in equation (4) leaves it identical in form, $J_2(\theta_0/T)$ is replaced by $J_2(\theta_N/T)$, where

$$\theta_N' = \cdot\, 2\theta_0 \tag{5}$$

The situation for the in-plane optical modes is not so simple. However, as an approximation, we will make the same kind of assumption, replacing θ_L and θ_T by

$$\left.\begin{aligned}\theta_M &= \sqrt{2}\theta_L\\ \theta_Q &= \sqrt{2}\theta_T\end{aligned}\right\} \tag{6}$$

(The square root occurs because of the particular wave-number-frequency relationship for the in-plane modes).

Figure 1 shows the magnitudes of the contributions to the thermal expansion coefficient α_a of the three acoustic modes given by equations (1), (2) and (3) and also the contributions of the acoustic plus optical modes [that is equations (1), (2) and (3)] evaluated with θ_0, θ_L and θ_T replaced by θ_N, θ_M and θ_Q) assuming that

$$\frac{1}{C_{11}}\left(\frac{\partial C_{11}}{\partial e_{xx}}\right) = \frac{1}{C_{11}-C_{12}}\,\frac{\partial(C_{11}-C_{12})}{\partial e_{xx}}$$

$$= \frac{1}{\delta}\left(\frac{\partial\delta}{\partial e_{xx}}\right) = 1 \tag{7}$$

Figure 1 shows that the inclusion of the optical mode contributions is important above 300–400°K.

In fact each mode will have a different value for the parameters equated in (7), and it is our problem to decide whether an appropriate choice of the parameters can reproduce the temperature dependence of α_a. It was speculated in a previous paper that $\delta^{-1}(\partial\delta/\partial e_{xx})$ might have a positive sign while $C_{11}^{-1}(\partial C_{11}/\partial e_{xx})$ and $(C_{11}-C_{12})^{-1} \times \partial(C_{11}-C_{12})/\partial e_{xx}$ are conventionally negative leading to a negative contribution to α_a from the out-of-plane mode and positive contributions from the in-plane modes. There is however, no direct evidence for the magnitude of these parameters. If we choose a Morse potential to represent the covalent nearest neighbour bonds in a layer plane then a simple calculation gives

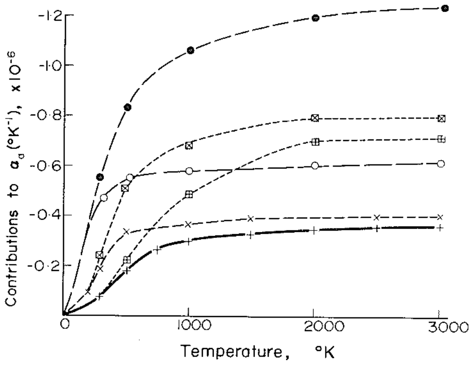

Fig. 1. 'Contributions to basal thermal expansion coefficient (with anharmonic coefficients equal to unity) as a function of temperature'.

+	'In-plane' longitudinal	Acoustic modes only
×	'In-plane' transverse	
○	Out-of plane	
⊞	'In-plane' longitudinal	Including optical modes
☒	'In-plane' transverse	
●	Out-of plane	

$$C_{11}^{-1}(\partial C_{11}/\partial e_{xx}) = -8{\cdot}2$$

The usual literature definition of the anharmonic coefficient is $\partial(\log\nu)/\partial(\log v)$ with a magnitude of 1–2, which leads to $\partial(\log\nu)/\partial e_{xx} \sim 3$–6, in reasonable agreement with our considerations. The value given above does not differ from that given in Ref [4], where the anharmonic coefficient for the in-plane longitudinal mode is defined as $[\gamma]_{xx} = \nu^{-1}\partial\nu/\partial e_{xx} = \frac{1}{2}C_{11}^{-1}(\partial C_{11}/\partial e_{xx}) = -4{\cdot}1$. In the ensuing calculation we assume that $(C_{11}-C_{12})^{-1}\partial(C_{11}-C_{12})/\partial e_{xx}$ has a value of $-8{\cdot}2$ also. The value of α_a is well known to be zero at about 400°C and since.

$$\alpha_a(T) = \alpha_1(T) + \alpha_2(T) + \alpha_3(T) \tag{8}$$

Equations (2), (3) and (4) combine to yield at that temperature (assuming acoustic and optical mode contributions):

$$0{\cdot}96\delta^{-1}(\partial\delta/\partial e_{xx}) = 8{\cdot}2(0{\cdot}35+0{\cdot}60)$$

or

$$\delta^{-1}(\partial\delta/\partial e_{xx}) = +8{\cdot}2 \qquad (9)$$

The variation of α_a with temperature can now be calculated using these values for the anharmonic coefficients. Table 2 gives a number of theoretical values of α_a at different temperatures and compares them with experimental data obtained from Bailey and Yates [9] and the analysis of a large amount of data by Morgan [10].

Table 2. Comparison of experimental and theoretical values of α_a at selected temperatures

Temperature (°K)	Theoretical α_a (°K^{-1})	Experimental α_a [9, 10] (°K^{-1})
200	$-1{\cdot}56\times10^{-6}$	$-1{\cdot}33\times10^{-6}$
300	$-1{\cdot}88$	$-1{\cdot}80$
1000	0·90	0·7
2000	1·64	1·3

A more detailed comparison of theory and experiment [9, 10] is shown in Fig. 2. It is clear that this theory, modelled on the first assumption described in the introduction, does give a reasonable explanation of the basal expansion coefficient numerically.

The theory presented is the simplest modification to the previous theories that will explain a negative component of the basal thermal expansion which is not due to the Poisson's ratio contraction associated with the large interlayer expansion. It has been assumed that the change in δ, the bond-bending force constant, with strain along the basal planes e_{xx} has the opposite sign to the other anharmonic coefficients. The out-of-plane vibrational mode involves the elastic moduli C_{44} and C_{33} and δ the bond-bending constant. As the temperature is reduced the bond bending component of the vibrations is frozen out, and the variations of C_{44} and C_{33} with e_{xx} become more important. If this surmise is correct, the anharmonic coefficient and therefore the basal expansion coefficient will become positive at low temperatures. The data of Bailey and Yates [9] suggest that this may occur below 30°K, although it does not show in their calculations of the moments of the anharmonicities.

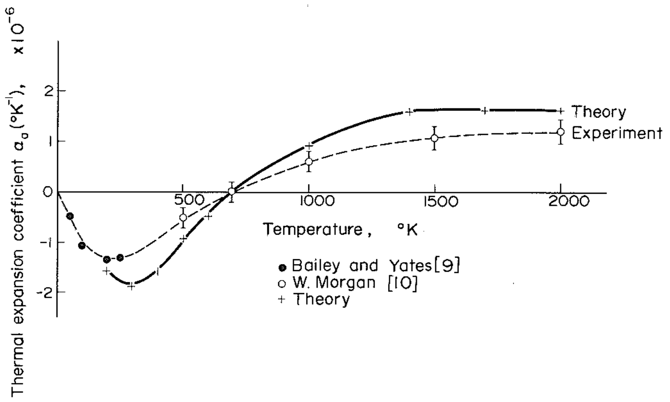

Fig. 2. Predicted basal expansion coefficient due to positive value of $\delta^{-1}(\partial\delta/\partial e_{xx})$ comparison of theory and experiment (no correction for Poisson's ratio effect of α_c).

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The major difficulty with this theory is the lack of any reason why $\delta^{-1}(\partial\delta/\partial e_{xx})$ should have a positive sign. The bond bending coefficient δ is not well understood theoretically (and this is perhaps the best reason for suspecting unusual behaviour) so that its behaviour is uncertain. An alternative possibility is described by Barron[7] who considers the increase in tension of bonds perpendicular to directions in a lattice with high vibration amplitudes as a source of negative thermal expansion in highly anisotropic lattices. This needs investigation before a final decision may be made regarding the basal expansion coefficient of graphite.

We are thus at present left with three alternative possibilities:

(a) The original explanation of the negative coefficient is correct and the direct measurements of S_{13}/S_{33} are incorrect.

(b) The bond-bending coefficient δ in the out-of-plane vibrational mode has a positive anharmonicity with respect to strains in the basal plane such that

$$\frac{1}{\delta}\cdot\frac{\partial\delta}{\partial e_{xx}} \approx 8$$

(c) The large vibrational amplitude in the out-of-plane direction produces a contraction by Barrons[7] mechanism.

The latter possibility will be the subject of a future paper.

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