

## THE THERMAL EXPANSION OF GRAPHITE WITHIN THE LAYER PLANES

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The thermal expansion of graphite within the layer planes has been investigated by X-ray diffractometer and powder diffraction techniques. Direct measurements of the  $a$  lattice dimension over the whole range of temperatures from  $-196^{\circ}\text{C}$  to  $3000^{\circ}\text{C}$  have been made for the first time. Two specimens were studied, one a spectroscopic electrode material of  $p \approx 0.2$  and the other a highly orientated pyrolytic graphite.

The variation of the coefficient of thermal expansion  $\alpha_a$  was computed from the measured variation with temperature of the  $a$  lattice dimension. It is shown that above about  $400^{\circ}\text{C}$  there is a progressive expansion of the interatomic spacings in the basal plane with  $\alpha_a$  approaching a limiting value of  $1.2 \times 10^{-6}$  per  $^{\circ}\text{C}$ . This provides the first experimental confirmation of theoretical prediction. Below  $400^{\circ}\text{C}$  there is an expansion with decrease in temperature. Below  $0^{\circ}\text{C}$  the rate of expansion rapidly decreases and a limiting value of the  $a$  lattice parameter is approached at  $-196^{\circ}\text{C}$ . These findings are consistent with the results of Nelson and Riley who found a minimum in the  $a$ -dimension at about  $400^{\circ}\text{C}$ .

The experimental data are compared with those predicted by theory and with those obtained by other workers.

La dilatation thermique du graphite suivant les plans de base de l'hexagone a été étudiée par les techniques du diffractomètre de rayon X et par celle des diagrammes de poudre. Des mesures directes du paramètre  $a$  ont été effectuées pour la première fois sur tout le domaine de températures depuis  $-196^{\circ}\text{C}$  à  $3000^{\circ}\text{C}$ . Deux échantillons ont été étudiés, l'un étant constitué par une électrode de spectroscopie de  $p \approx 0,2$  et l'autre provenant d'un graphite pyrolytique fortement orienté.

La variation du coefficient de dilatation thermique  $\alpha_a$  fut déterminée à partir des variations mesurées du paramètre réticulaire  $a$  en fonction de la température. On a ainsi montré qu'au dessus de  $400^{\circ}\text{C}$  environ, il y a une dilatation progressive des distances interatomiques dans le plan basal conduisant à une valeur

limite du coefficient  $\alpha_a$  égale à  $1,2 \times 10^{-6}$  par  $^{\circ}\text{C}$ . Ceci apporte la première confirmation expérimentale de prévisions théoriques. En-dessous de  $400^{\circ}\text{C}$  il y a une dilatation en fonction de la température décroissante. En dessous de  $0^{\circ}\text{C}$ , la vitesse de dilatation diminue rapidement et le paramètre réticulaire  $a$  atteint une valeur limite aux environs de  $-196^{\circ}\text{C}$ . Ces constatations sont en accord avec les résultats de Nelson et Riley qui trouvèrent un minimum pour le paramètre  $a$  à environ  $400^{\circ}\text{C}$ .

Les données expérimentales sont comparées à celles prédites par la théorie ou avec celles obtenues par d'autres auteurs.

Die thermische Ausdehnung von Graphit in Flächenschichten wurde mit Hilfe des Röntgendiffraktometers und von Pulverbeugungsmethoden untersucht. Direktmessungen des Gitterparameters  $a$  wurden über den Temperaturbereich von  $-196^{\circ}\text{C}$  bis  $3000^{\circ}\text{C}$  gemacht. Zwei Proben wurden untersucht; die eine davon war spektroskopisches Elektrodenmaterial mit  $p \approx 0,2$ , die andere ein hochorientierter pyrolytischer Graphit.

Die Änderung des Wärmeausdehnungskoeffizienten  $\alpha_a$  wurde aus der gemessenen Änderung des Gitterparameters  $a$  mit der Temperatur berechnet. Es wurde gezeigt, dass oberhalb  $400^{\circ}\text{C}$  eine progressive Ausdehnung der interatomaren Räume in der Grundfläche stattfindet, wobei der Grenzwert für  $\alpha_a$  etwa  $1,2 \times 10^{-6}$  pro  $^{\circ}\text{C}$  ist. Diese Tatsache liefert die erste experimentelle Bestätigung theoretischer Voraussagen. Oberhalb  $400^{\circ}\text{C}$  nimmt die Ausdehnung mit der Temperatur ab. Unterhalb  $0^{\circ}\text{C}$  sinkt der Ausdehnungskoeffizient rasch und ein Grenzwert des Gitterparameters  $a$  wird bei  $-196^{\circ}\text{C}$  angenähert erreicht. Diese Ergebnisse sind mit denen von Nelson und Riley vereinbar. Beide fanden ein Minimum der  $a$ -Dimension bei etwa  $400^{\circ}\text{C}$ .

Die experimentellen Daten werden mit denen verglichen, die sich aus der Theorie ergeben und mit den Werten, die durch andere Autoren erhalten worden sind.

## 1. Introduction

A great deal of interest has been shown recently in the thermal expansion of graphite, in connection with studies of mechanical properties and behaviour on neutron irradiation. An investigation has already been reported <sup>1)</sup> of the thermal expansion behaviour of various carbon materials perpendicular to the graphite layer planes.

Riley <sup>2)</sup> derived theoretically the form of the curve representing the variation with temperature of the thermal expansion coefficient within the layer planes,  $\alpha_a$ . The form of this curve has been confirmed and further developed by Sutton and Howard <sup>3)</sup> and Entwisle <sup>4)</sup> who have based their predictions on macroscopic thermal expansion measurements on bulk graphite.

Not since the work of Nelson and Riley <sup>5)</sup> in 1945, however, has any direct measurement been made of the variation with temperature of the  $a$  lattice parameter in graphite. The change in the  $a$ -dimension then observed ( $\sim 0.0005$  Å over the range  $+15^\circ\text{C}$  to  $800^\circ\text{C}$ ) was only slightly greater than the experimental error. The recent development of special apparatus in our Laboratories and the availability of suitable specimens has enabled further progress to be made.

Low-temperature and high-temperature attachments developed <sup>6)</sup> for the Philips PW1050 diffractometer, together with a conventional high-temperature powder camera, were used for the work, to enable the whole range of temperatures from  $-196^\circ\text{C}$  to  $3000^\circ\text{C}$  to be covered for the first time. A highly orientated pyrolytic graphite was also available, from which diffractometer specimens could be sliced in a direction to enhance the required X-ray reflexions. A spectroscopic electrode graphite ( $p \simeq 0.2$ ) was examined over the range  $1200^\circ\text{C}$  to  $3000^\circ\text{C}$ .

It is assumed throughout that the  $a$ -dimension does not vary significantly with crystal perfection, because the  $a$ -dimensions at room temperature of several artificial graphites, varying in degree of crystal perfection from  $p \simeq 0.019$  to  $p \simeq 0.2$  have been shown <sup>7,8)</sup> to

be identical. The parameter  $p$  denotes the degree of disorder or more exactly the proportion of misoriented layers of carbon atoms. A good-quality natural graphite has a  $p$  factor near zero, whilst a coke made by low-temperature carbonization of, say, cellulose will have a  $p$  parameter near unity.

## 2. Theory

In 1924 Grüneisen and Goens <sup>9)</sup> derived a theory of the thermal expansion of anisotropic (hexagonal) crystals at low temperatures (i.e. below about  $300^\circ\text{K}$ ) which enabled them to correlate the expansion data for zinc and cadmium with the elastic moduli and heat capacities. Riley <sup>2)</sup> extended this theory so that it was not restricted to low temperatures, and applied it to the data for graphite. The heat-capacity quantities used by Riley are more simply defined and are easily obtainable from experimental data usually available.

Riley showed that during thermal expansion the graphite lattice is effectively being stretched in one direction only (because the expansion in the direction parallel to the  $c$  axis is many times larger than that within the layer planes) and a lateral contraction, given by Poisson's ratio and proportional to  $S_{13}$ , will accompany the stretching. At low temperatures the lateral contraction will be greater than the small thermal expansion within the layers and therefore  $\alpha_a$  will be negative. At some temperature,  $T_m$  thermal expansion exactly balances the Poisson contraction and  $\alpha_a = 0$ . Above  $T_m$ ,  $\alpha_a$  will be positive and increase with temperature.

In the usual notation, Riley has that

$$\alpha_a = \frac{1}{a} \left( \frac{\partial a}{\partial T} \right)_p \quad (1a)$$

$$\alpha_c = \frac{1}{c} \left( \frac{\partial c}{\partial T} \right)_p \quad (1b)$$

Defining entropy as

$$S = \int_0^T \frac{c_p}{T} dT,$$

and introducing elastic moduli  $S_{11}$ ,  $S_{12}$ ,  $S_{13}$  and

$S_{33}$  it can be shown that

$$\alpha_a = (S_{11} + S_{12})q_a + S_{13}q_c \quad (2a)$$

$$\alpha_c = 2 S_{13}q_a + S_{33}q_c \quad (2b)$$

where  $q_a$  and  $q_c$  are the so-called "thermal pressure coefficients", perpendicular and parallel to the hexagonal axis. They are of the form

$$q_{a,c} = \frac{1}{V} \int_0^T \left( \frac{\partial C_p}{\partial \log(a,c)} \right) \frac{dT}{T} \quad (3)$$

where  $V$  is the gram-atomic volume, and  $C_p$  is the heat capacity at constant pressure per gram-atom.

To evaluate  $q_a$  and  $q_c$  as functions of temperature, the quantum theory of specific heats must be used. The heat capacities are expressed as Debye functions and the thermal pressure coefficients are expressed in a form suitable for evaluation. Substitution of these values into eq. (2a) gives the final form of the expression for the coefficient of thermal expansion perpendicular to the hexagonal axis:

$$\alpha_a = AC_{Va} + BC_{Vc} + CT \quad (4)$$

where  $C_{Va}$  and  $C_{Vc}$  are the two components of the heat capacity at constant volume, perpendicular and parallel respectively to the hexagonal axis, and where  $A$ ,  $B$  and  $C$  are constants. The constant  $C$  contains positive and negative components ( $S_{13}$  is negative), both of which are of the same order of magnitude. Consequently the term directly proportional to the temperature can be neglected.

Hence:

$$\alpha_a = AC_{Va} + BC_{Vc}. \quad (5)$$

Integration of eq. (5) leads to the following expression in  $a$ :

$$\log a = AU_a + BU_c + \log a_0 \quad (6)$$

where  $a_0$  is the value of  $a$  at absolute zero, and where  $U_a$  and  $U_c$ , being the integrals of  $C_{Va}$  and  $C_{Vc}$ , are components of the internal energy  $U$ .  $U_a$  and  $U_c$  can be evaluated by expressing them in terms of the Debye energy functions which have been tabulated by Beattie<sup>10</sup>.

The problem now is to choose values for  $A$ ,  $B$  and  $a_0$  which give the best agreement with the experimental data. From the values of the constants  $A$  and  $B$ , a plot of  $\alpha_a$  against temperature can be derived from eq. (5) using Beattie's tables to evaluate  $C_{Va}$  and  $C_{Vc}$ .

At very high temperatures, the Debye functions approach unity. For graphite this condition is reached approximately when  $T > 2000^\circ \text{K.}$  Above this temperature

$C_V \doteq C_{Va} \doteq C_{Vc} \doteq 3R$  where  $R$  is the gas constant.

Hence the expansion coefficient can be expressed approximately as a linear function of  $T$ :

$$\alpha_a = (A + B) 3R + CT.$$

In this case, if  $C$  is negligible,  $\alpha_a$  is approximately constant at very high temperatures, and has a value of about  $(A + B)3R$ . Riley<sup>2</sup>) computed this value to be about  $1.5 \times 10^{-6}$ .

### 3. Previous Experimental Work

The only other known experiments directed to measuring the changes with temperature of the  $a$ -dimension in graphite have been those of Nelson and Riley<sup>5</sup>), Matuyama<sup>11</sup>) and Micinski<sup>12</sup>). Comparison of their results is shown in table 1.

Pierrey<sup>13</sup>) and others have used dilatometric methods to obtain coefficients of expansion. Pierrey measured dimensional changes in directions parallel to and perpendicular to the pressing direction in compacts made from graphite flakes. Lack of precise knowledge of the degree of preferred orientation, however, makes interpretation of such results difficult, because small changes in the  $a$ -dimension are overridden by components of the much larger expansion in the  $c$  direction.

Micinski used a macroscopic measuring technique (an interferometer method), on specimens selected as having a particularly striated appearance. His measurements were made parallel and perpendicular to these striations, but the precise nature of the striations was not stated. The material used comprised particles of  $3000^\circ \text{C}$  heat-treated petroleum coke, and the thermal

TABLE I  
Comparison of previously determined experimental data

Author(s)	Coefficient of thermal expansion in the $a$ -direction $\alpha_a$ (per °C)	Temperature range (°C)	Type of graphite used
Micinski <sup>12)</sup> (1955) . . . . .	$-0.65 \times 10^{-6}$ 0 Positive	0–150 c. 250 ( $=T_m$ ) 250–	3000° C heat-treated petroleum coke particles
Matuyama <sup>11)</sup> (1954) . . . . .	$+0.95 \times 10^{-6}$	1000–1800	Ceylon graphite
Nelson and Riley <sup>5)</sup> (1945) . .	$-1.5 \times 10^{-6}$ 0 $+0.9 \times 10^{-6}$	0–150 c. 400 ( $=T_m$ ) 600–800	Ceylon graphite

expansion coefficient of the particles became zero at about 250° C and became positive above this temperature.

Matuyama, using a high-temperature Debye-Scherrer camera fitted with a small carbon-tube furnace, confined his measurements to a determination of the value of the  $a$ -dimension at 1800° C.

Nelson and Riley used a high-temperature 19 cm diameter powder camera and X-ray photographs were taken at the following temperatures: 14.6° C, 150° C, 300° C, 450° C, 600° C, 700° C and 800° C. The films were measured independently by each author, and the best extrapolated  $a$ -value taken (see fig. 1). From the measurements they obtained the following values for the constants  $A$ ,  $B$  and  $a_0$  in eq. (6).

$$A = 0.1620 \times 10^{-13}$$

$$B = -0.1013 \times 10^{-13}$$

$$a_0 = 2.46165 \text{ \AA}$$

Substituting the numerical values of  $A$  and  $B$  in eq. (5), they were able to plot the variation with temperature of the thermal expansion coefficient perpendicular to the hexagonal axis (see fig. 2). Their value of the  $a$ -dimension at 15° C was  $2.46117 \pm 0.0001 \text{ \AA}$ .

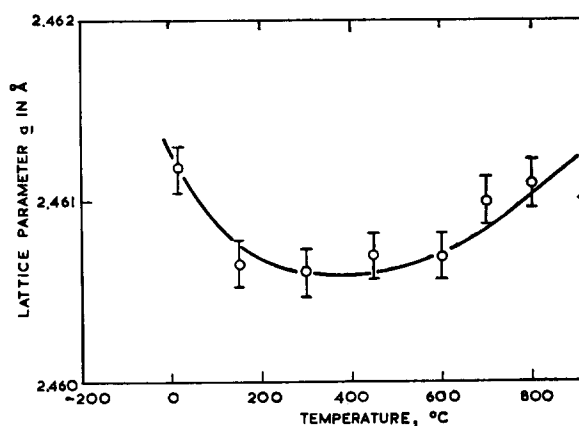


Fig. 1. The results of Nelson and Riley. The variation with temperature of the  $a$ -dimension.

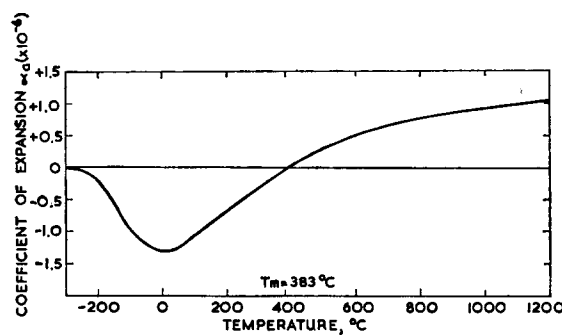


Fig. 2. The results of Nelson and Riley. The theoretical variation with temperature of the coefficient of thermal expansion perpendicular to the hexagonal axis,  $\alpha_a$ .

#### 4. Experimental

The basis of the method employed in the present work was the measurement of the variation of the peak position of a given diffraction maximum with change in temperature. The complete range of temperatures covered can be divided conveniently into three parts, according to the method of obtaining the temperature required and of recording the required diffraction maxima. Some overlap between the three parts provided a useful means of cross-checking results.

##### 4.1. RANGE OF TEMPERATURES FROM $-196^{\circ}\text{C}$ TO $+55^{\circ}\text{C}$

The low-temperature attachment for a Philips PW1050 diffractometer, previously designed<sup>6)</sup> for the measurement of the much larger thermal expansion of graphite perpendicular to the basal planes, was used for this range.

The specimens which were in rod form, of dimensions  $10 \times 2 \times 1.5$  mm were made from a highly orientated pyrolytic graphite ( $p \simeq 0.1$ ) which had been graphitised at  $2980^{\circ}\text{C}$ . The rods had been cut so that the basal planes were parallel to the smaller ( $10 \times 1.5$  mm) sides. This enabled the maximum possible intensity to be obtained from cross-lattice reflexions using a larger side ( $10 \times 2$  mm) as the "reflecting" surface. Two such specimen rods were mounted side by side in a conventional specimen holder and a copper-eureka thermocouple placed in holes drilled laterally through them (fig. 3).

Observations were confined to the  $11\bar{2}0$  and

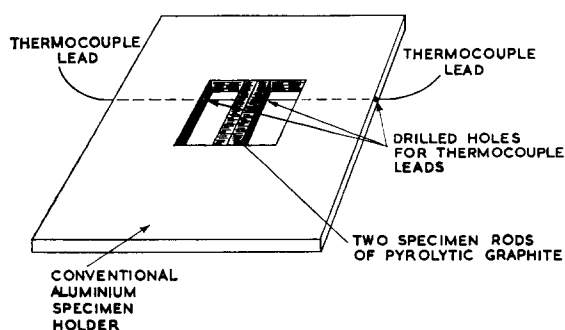


Fig. 3. Specimen and holder for low-temperature attachment for the Philips PW 1050 diffractometer.

$10\bar{1}0$  reflexions. The time taken to record each reflexion was approximately ten minutes. At each temperature, the diffraction line profile was recorded several times and the average peak position obtained. Temperature fluctuations during the recording of any reflexion were less than  $\pm 10^{\circ}\text{C}$ , and, as in the earlier work<sup>1)</sup> with this apparatus, no specimen movement was detected during the experiments. After each temperature cycle, measurements at room temperature were repeated to eliminate possible systematic errors.

A few measurements above ambient temperature were made by passing a stream of warm air continuously over the specimen holder. These provided some overlap with the next temperature range.

Although the "fixed time counts" technique is potentially capable of a higher statistical accuracy than the pen-recorder trace, it was not used because ice formation on the specimen became excessive during the longer time required.

##### 4.2. RANGE OF TEMPERATURES FROM $18^{\circ}\text{C}$ TO $1250^{\circ}\text{C}$

A conventional 19 cm diameter high-temperature Debye-Scherrer vacuum powder camera was used to cover this range of temperatures. Flakes of the highly orientated pyrolytic graphite ( $p \simeq 0.1$ ), cut into thin rods and mounted in alumina paste, made convenient specimens.

X-ray photographs, using unfiltered copper radiation to reduce exposure times, were taken at the following temperatures:  $18^{\circ}\text{C}$ ,  $150^{\circ}\text{C}$ ,  $200^{\circ}\text{C}$ ,  $350^{\circ}\text{C}$ ,  $550^{\circ}\text{C}$ ,  $650^{\circ}\text{C}$ ,  $800^{\circ}\text{C}$ ,  $900^{\circ}\text{C}$ ,  $1100^{\circ}\text{C}$  and  $1250^{\circ}\text{C}$ . Measurements were made of the  $10\bar{1}0_{\alpha}$ ,  $11\bar{2}0_{\alpha}$ ,  $11\bar{2}0_{\beta}$ ,  $12\bar{3}0_{\alpha_1}$  and  $12\bar{3}0_{\alpha_2}$  diffraction peak positions. In order to obtain the best value for the  $a$ -dimension at each temperature, the apparent  $a$  values derived from the measurement of the above lines were plotted against the well-known Nelson and Riley extrapolation function

$$\left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right).$$

Although the  $10\bar{1}0_x$  line was measured, little weight was assigned to this value in the extrapolation.

As explained by Nelson and Riley<sup>5)</sup> the refraction correction for  $a$  is negligible in comparison with the probable experimental error, which is approximately one part in 3000. The error in temperature measurement did not exceed  $\pm 25^\circ\text{C}$  at the highest temperature investigated and was less than this at lower temperatures.

#### 4.3. RANGE OF TEMPERATURES FROM $1000^\circ\text{C}$ TO $3000^\circ\text{C}$

An attachment for a Philips PW1050 diffractometer, described elsewhere<sup>6)</sup>, was used to record the required diffraction peaks throughout the range of temperatures  $1000^\circ\text{C}$  to  $3000^\circ\text{C}$ .

The specimens were in rod form, of dimensions  $26 \times 1 \times 0.5$  mm. Two materials were examined:

- (i) a sample of spectroscopic carbon rod,  $p \simeq 0.2$ , with little preferred orientation,
- (ii) a sample of pyrolytic material,  $p \simeq 0.1$ , with a high degree of preferred orientation, which had been graphitised at  $2980^\circ\text{C}$ .

Observations were confined to the  $(11\bar{2}0)$  reflexions, plotted on the usual pen-recorder trace. The time taken to record each trace was approximately ten minutes, and throughout the runs, both at room temperature and at elevated temperatures, the specimen enclosure was filled with argon at constant pressure. Observations at room temperature were made before and after each temperature cycle.

Temperature measurements were made using an optical pyrometer, with appropriate corrections for emissivity and absorption in windows. For each specimen, temperature fluctuations during the recordings were less than  $\pm 10^\circ\text{C}$ . It was noticed during observations on specimen (ii) that the temperature of the specimen surface parallel to the layer planes, as measured by the pyrometer, was lower than that of the surface at right angles to this direction. It has not been established whether

this difference is one of emissivity or actual temperature. It is possible that the extreme anisotropy of the specimen would produce a real temperature difference between centre and surface of the specimen.

The diffraction profiles, obtained using both high and low-temperature attachments for the diffractometer, showed little  $K_{\alpha_1\alpha_2}$  doublet resolution and no attempt was made to separate these two components.

## 5. Results

Values of the  $a$ -dimension in the range of temperatures  $-196^\circ\text{C}$  to  $+55^\circ\text{C}$  derived from the diffraction maxima peak positions, are given in table 2, together with the "corrected" values of the angle  $2\theta$  for the  $11\bar{2}0$  diffraction maximum. Tables 3 and 4 list corresponding values in the temperature ranges  $18^\circ\text{C}$  to

TABLE 2

Variation with temperature of the  $a$  lattice parameter of graphite in the range of temperatures  $-196^\circ\text{C}$  to  $+55^\circ\text{C}$  (determined using the low-temperature attachment for a Philips PW1050 diffractometer)

Graphite specimen	Temperature ( $^\circ\text{C}$ )	"Corrected" $2\theta_{11\bar{2}0}$	$a$ ( $\text{\AA}$ )
Rod of $3000^\circ\text{C}$ pyrolytic graphite ( $p \simeq 0.1$ )	$-196$	77.479	2.4617
"	$-196$	77.477	2.4618
"	$-196$	77.482	2.4616
"	$-170$	77.485	2.4616
"	$-170$	77.488	2.4615
"	$-150$	77.490	2.4615
"	$-140$	77.489	2.4615
"	$-120$	77.480	2.4617
"	$-115$	77.491	2.4614
"	$-110$	77.492	2.4614
"	$-100$	77.496	2.4613
"	$-80$	77.487	2.4615
"	$-60$	77.490	2.4614
"	$-32$	77.494	2.4613
"	$+40$	77.507	2.4610
"	$+55$	77.510	2.4609

With this attachment the accuracy of temperature measurement is estimated to  $\pm 5^\circ\text{C}$ , and the  $a$ -dimension to be accurate within  $\pm 0.0001 \text{ \AA}$ .

TABLE 3

Variation with temperature of the  $a$  lattice parameter of graphite in the range of temperatures 18° C to 1250° C (determined using a high temperature Debye-Scherrer powder camera)

Graphite specimen	Temperature (°C)	Extrapolated $a$ -value (Å)
Sliced flake of pyrolytic graphite ( $p \approx 0.1$ )	18	2.4612
"	150	2.4605
"	200	2.4605
"	350	2.4607
"	550	2.4605
"	650	2.4610
"	800	2.4612
"	900	2.4617
"	1100	2.4618
"	1250	2.4620

Using this camera, the accuracy of temperature measurement is estimated to be  $\pm 2\%$ , and the  $a$ -dimension to be accurate within  $\pm 0.0002$  Å.

1250° C and 900° C to 3000° C respectively. The variation with temperature of the  $a$ -dimension for all the temperatures investigated is shown explicitly in fig. 4.

It may be seen from fig. 4 that above about 400° C there is a regular expansion of atomic spacings within the layer planes. Below this

TABLE 4

Variation with temperature of the  $a$ -lattice parameter of graphite in the range of temperatures 900° C to 3000° C (determined using the high-temperature attachment for the Philips diffractometer)

Graphite specimen	Temperature (°C)	"Corrected" $2\theta_{11\bar{2}0}$	$a$ (Å)
Spectroscopic graphite ( $p \approx 0.2$ )	1575	77.425	2.4632
"	1625	77.420	2.4633
"	1943	77.396	2.4640
"	2116	77.382	2.4643
"	2310	77.349	2.4652
"	2375	77.356	2.4650
"	2522	77.322	2.4659
"	2783	77.301	2.4665
"	3054	77.255	2.4679
Pyrolytic graphite ( $p \approx 0.1$ )	892	77.480	2.4616
"	1215	77.460	2.4622
"	1312	77.450	2.4625
"	1409	77.425	2.4632
"	1470	77.447	2.4626
"	1558	77.434	2.4629
"	1743	77.405	2.4637
"	1862	77.397	2.4639

With this attachment, the accuracy of temperature measurement is estimated to be  $\pm 2\%$ , and the  $a$ -dimension to be accurate within  $\pm 0.0002$  Å.

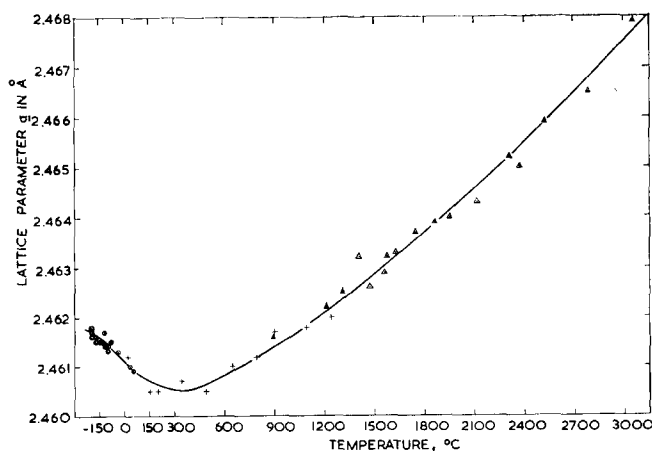


Fig. 4. Variation with temperature of the  $a$ -dimension. Measurements made with:

- low-temperature device for diffractometer
- + high-temperature powder camera
- △ high-temperature device for diffractometer.

temperature there is also an expansion with decrease in temperature. As the temperature is lowered below  $0^{\circ}\text{C}$  however, the rate of expansion rapidly decreases and a saturation condition is approached. The  $a$ -dimension shows a minimum between  $350^{\circ}\text{C}$  and  $400^{\circ}\text{C}$ . This is consistent with the results of Nelson and Riley <sup>5)</sup> who found a minimum in the  $a$ -dimension at about  $400^{\circ}\text{C}$  and also with the theory

of Riley <sup>2)</sup> which predicted a minimum at  $383^{\circ}\text{C}$ .

For the high-temperature range ( $1200^{\circ}\text{C}$ – $1800^{\circ}\text{C}$ ), over which observations were made

TABLE 5

	Present results	Nelson and Riley <sup>5)</sup>
$A$	$0.1777 \times 10^{-13}$	$0.1620 \times 10^{-13}$
$B$	$-0.1065 \times 10^{-13}$	$-0.1013 \times 10^{-13}$
$a_0 (\text{\AA})$	2.46169	2.46165

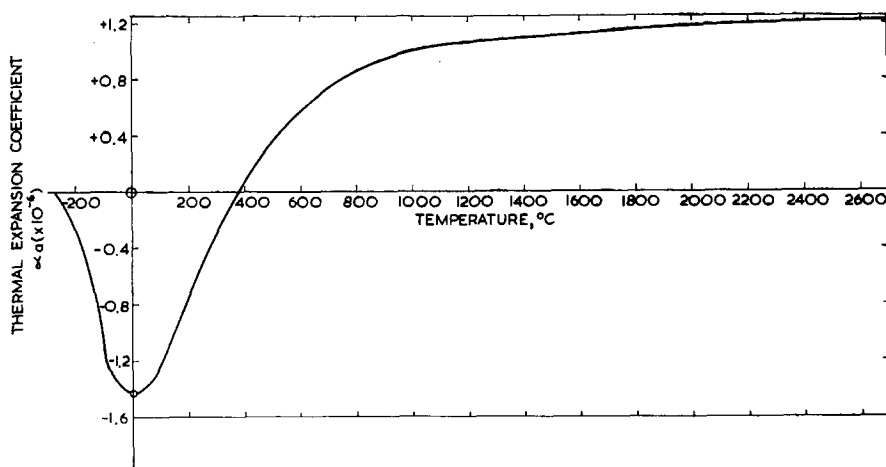


Fig. 5. Observed variation with temperature of the coefficient of thermal expansion perpendicular to the hexagonal axis,  $\alpha_a$ .

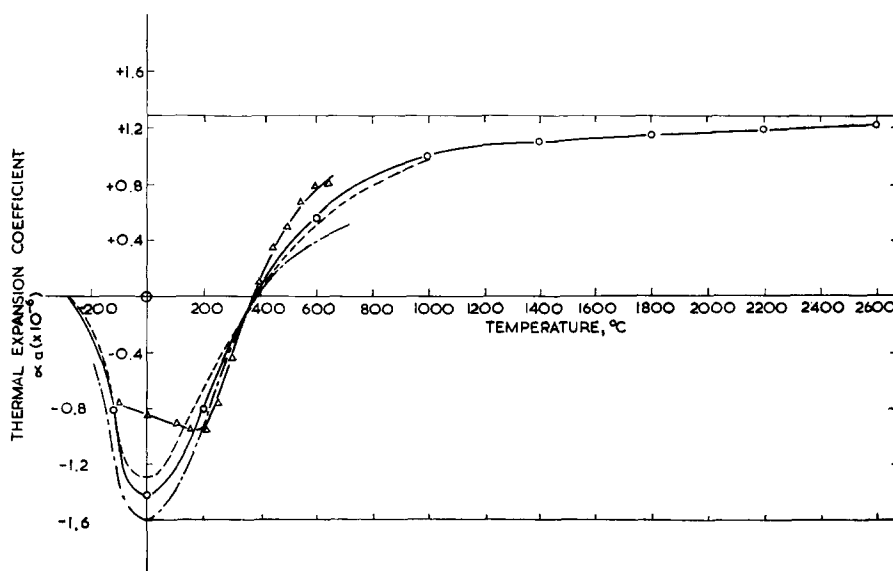


Fig. 6. Variation with temperature of the coefficient of thermal expansion perpendicular to the hexagonal axis. Comparison with previous measurements.

— Sutton and Howard (1962).  
 -△—△- Entwisle (1962).

----- Nelson and Riley (1945).  
 -○—○- Present work (1963).



on both samples, no difference was detectable in the behaviour of the two samples, although there is a difference in perfection between these samples.

Using the present experimental data over the range of temperatures  $-196^{\circ}\text{C}$  to  $+3000^{\circ}\text{C}$  values for the constants  $A$ ,  $B$  and  $a_0$  were derived by substitution in eq. (6). These values are compared in table 5 with those obtained by Nelson and Riley<sup>5)</sup> in the range of temperatures  $15^{\circ}\text{C}$  to  $800^{\circ}\text{C}$ .

Substitution of these values of  $A$  and  $B$  in eq. (5) yielded a curve of the variation with temperature of the thermal expansion coefficient perpendicular to the hexagonal axis  $\alpha_a$ . This curve (fig. 5) was in substantially complete agreement with that computed directly from the slope of the curve of the variation with temperature of the  $a$ -dimension. In fig. 6 the curve is compared with that computed by Nelson and Riley and with those predicted by Sutton and Howard<sup>3)</sup> and by Entwisle<sup>4)</sup>.

The present results of the variation with temperature of the  $a$  lattice parameter agree extremely well with those obtained by Nelson and Riley<sup>5)</sup> over the temperature range ( $15^{\circ}\text{C}$  to  $800^{\circ}\text{C}$ ) of their investigation; they are also in good agreement with the form of the variation as predicted by the theory of Riley<sup>2)</sup>. In particular the thermal expansion coefficient

appears to be asymptotic to a value of  $1.2 \times 10^{-6}$  per  $^{\circ}\text{C}$  at very high temperatures.

As may be seen from fig. 6, the present curve of the variation with temperature of the thermal expansion coefficient,  $\alpha_a$ , agrees in all essentials with that predicted by Riley, and by Sutton and Howard<sup>3)</sup>.

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