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THERMAL EXPANSION COEFFICIENTS OF GRAPHITE CRYSTALS*

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ABSTRACT

Graphite crystal expansions were derived as a function of temperature using the theoretical relationships of Riley$^{(1)}$; the resultant equations provide reasonable fits to the measured lattice expansion data over the temperature range 300° to 3000°K.

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DISCLAIMER

INTRODUCTION

In 1924, Gruneisen and Goens(2) derived a theory on the relationships between thermal expansion, elastic moduli and heat capacities of hexagonal crystals at low temperatures; in 1945, Riley(1) extended this theory to higher temperatures and with specific application to graphite. A significant amount of additional data, especially in regard to thermal expansion at higher temperatures, has become available since publication of Riley's results; this paper presents the results of an analysis of currently available data, undertaken to obtain improved estimates of the lattice thermal expansion coefficients of graphite.

THEORY

Riley has shown(1) that the heat capacity at constant volume, C_V, for a graphite crystal can be considered as composed of two components:

$$C_V = \frac{2}{3} C_{V_a} + \frac{1}{3} C_{V_c} . \tag{1}$$

The components, C_{V_a} and C_{V_c} refer to vibrations parallel and perpendicular to the basal planes, respectively, and are expressible by the Debye functions

$$C_{V_a} = 3\ RD(\frac{\theta_a}{T}); \quad C_{V_c} = 3\ RD(\frac{\theta_c}{T}). \tag{2}$$

where θ_a and θ_c are the characteristic temperatures associated with the lattice vibrations, T is the absolute temperature of measurement and R is the ideal gas constant.

The heat capacity at constant pressure, C_p, can be written in terms of the well-known relationship

$$C_p = C_V + \frac{\alpha_V{}^2 V\ T}{K} \tag{3}$$

where α_V is the volumetric coefficient of thermal expansion, V is the molar volume, and K is the volumetric compressibility. Since the temperature variations of α_v and K are of the same order of magnitude, Riley assumed that the ratio of α_v^2/K could be approximated by a constant, G, and the two components of the heat capacity then written as

$$C_{p_a} = C_{v_a} + G_a VT; \; C_{p_c} = C_{v_c} + G_c VT \tag{4}$$

where the constants G_a and G_c are defined by the relationship

$$G = \frac{2}{3} \; G_a + \frac{1}{3} G_c. \tag{5}$$

The crystal lattice coefficients of thermal expansion, α_a and α_c parallel and perpendicular to the basal planes were shown to be expressible in convenient form as:

$$\alpha_a = A \, C_{v_a} + B \, C_{v_c} + CT, \tag{6a}$$

$$\alpha_c = L \, C_{v_a} + M \, C_{v_c} + NT, \tag{6b}$$

where

$$A = \frac{2}{3} \; \frac{\gamma_a}{V} (s_{11} + s_{12}) \tag{7a}$$

$$B = \frac{1}{3} \; \frac{\gamma_c}{V} \; s_{13} \tag{7b}$$

$$L = \frac{4}{3} \; \frac{\gamma_a}{V} \; s_{13} \tag{7c}$$

$$M = \frac{1}{3} \; \frac{\gamma_c}{V} \; s_{33} \tag{7d}$$

$$C = \frac{1}{3} [2 \, G_a (s_{11} + s_{12}) + G_c \, s_{13}] \tag{7e}$$

$$N = \frac{1}{3} [4 \, G_a \, s_{13} + G_c \, s_{33}] \tag{7f}$$

s_{11}, s_{12}, s_{13} and s_{33} are crystal elastic moduli and A, B, C, L, M and N are treated as constants.

Integrations of equations 6a and 6b yields the equations

$$\ln \left(\frac{a}{a_o}\right) = A \, U_a + B \, U_c + \frac{C}{2} T^2 \tag{8a}$$

$$\ln \left(\frac{c}{c_o}\right) = L \, U_a + M \, U_c + \frac{N}{2} T^2 \tag{8b}$$

where a and c are the crystal lattice a- and c- spacings at temperature, T,

a_o and c_o are the lattice spacings at T = 0°K,

$U_a = 3\ RT\ F(\frac{\theta a}{T})$, $U_c = 3\ RT\ F(\frac{\theta c}{T})$, and

$F(\frac{\theta}{T})$ are the Debye functions, which have been numerically evaluated and tabulated by Beattie.(3)

The Debye Temperatures for Graphite

Riley used the Debye Temperatures derived by Magnus(4) from specific heat measurements made over the temperature range 44 to 1100°K.

A considerable amount of specific heat data has been accumulated since that time and various analyses have been made to derive Debye temperatures from the data; however, the primary emphasis has been on explaining the characteristic features of the specific heat curve at low temperatures(5,6). Because of this difference in emphasis and the lack of agreement on Debye temperatures, it was deemed preferable to derive the Debye temperatures using the best available specific heat data over the temperature range of interest in this study.

McDonald(7) has recently made precision measurements of heat content and derived the specific heats of graphite over the temperature range 300 to 1800°K; these data match well with the data of DeSorbo and Tyler(8) taken below 300°K. Moreover, except for differences of 2-3% near room temperature, these two sets of data are in excellent agreement with NBS evaluations(9,10) of previous specific heat data.

The combined data of DeSorbo and Tyler(8) and McDonald(7) were reduced to specific heat at constant volume using the approximation:

$$C_v = C_p' (1 - \delta C_p' T), \qquad (9)$$

$$C_p' = C_p - \gamma T, \text{ and}$$

$$\delta = \frac{\alpha_v^2 V}{K(C_p')^2}, \text{ evaluated at room temperature.}$$

The coefficient of volumetric thermal expansion, $\alpha_V = 22.9 \times 10^{-6}$ was obtained from Riley's(1) theoretical analysis; the molar volume, V, was taken as 5.31 cm^3/mole; the value used for the isothermal compressibility, $K = 29.6 \times 10^{-12}$ cm^2/dyne is that recomputed by Gschneidner(11) from the measurements of Bridgman(12); the electronic heat constant, $\gamma = 3.3 \times 10^{-6}$ cal/mole, is from the measurements of Kessom and Van der Hoeven(13).

Analysis of the data, using the numerical evaluations of the Debye functions, $D(\frac{\theta}{T})$, tabulated by Beattie(3), resulted in a best fit with Debye temperatures of θ_c = 800°K and θ_a = 2300°K. It should be noted that in order to verify the significance of these Debye temperatures, the author performed a least-squares regression analysis for each of the other eight permutations of the set $\theta_c = 800 \pm 10$°K, $\theta_a = 2300 \pm 10$°K. The variance between calculated and measured specific heats was significantly increased in all cases; thus, the author believes that one might sensibly attach an uncertainty of only ± 5°K to these Debye temperatures. The specific heats calculated for temperatures below about 400°K are especially dependent on the Debye temperatures and it was impossible to simultaneously obtain a good fit to data below 100°K and data taken above about 200°K.

In Table I, the calculated specific heats are compared with measured and evaluated tabulations; the largest differences being less than 4% at 150°K. However, the differences increase below 150°K; the calculated specific heat being about 10% below the measured values at 125°K and 25% low at 100°K. These differences evidently chronicle the beginning of the transition of the specific heat from the Debye T^3 dependence to the well known T^2 dependence, which is observed from approximately 15° to 50°K(8).

TABLE I

Specific Heat of Graphite
(in units of calories/mole)

	Calculated Specific Heat				Measured C_p		Previous Compliations	
Temperature °K	C_{v_a}	C_{v_c}	C_v	C_p	(a)	(b)	NBS#1 (c)	NBS#2 (d)
150	0.129	1.972	0.743	0.744	0.772			0.767
175	0.204	2.519	0.976	0.977	0.980			
200	0.302	2.999	1.201	1.204	1.190			1.190
225	0.425	3.409	1.419	1.432	1.406			
250	0.570	3.753	1.631	1.636	1.629			1.632
275	0.735	4.042	1.837	1.843	1.843			
300	0.916	4.282	2.038	2.046	2.053	2.05	2.071	2.083
400	1.720	4.921	2.787	2.806		2.82	2.85	2.85
500	2.496	5.263	3.418	3.454		3.49	3.49	3.50
600	3.149	5.464	3.921	3.976		4.03	3.99	4.03
700	3.669	5.590	4.309	4.388		4.44	4.39	4.43
800	4.075	5.674	4.608	4.710		4.74	4.72	4.75
900	4.392	5.736	4.840	4.967		4.97	4.97	4.75
1000	4.640	5.775	5.019	5.171		5.15	5.16	5.14
1100	4.838	5.807	5.161	5.338		5.30	5.30	5.27
1200	4.996	5.831	5.274	5.477		5.43	5.42	5.42
1300	5.124	5.850	5.366	5.594		5.56	5.52	5.57
1400	5.229	5.865	5.441	5.694		5.67	5.61	5.67
1500	5.316	5.878	5.503	5.782		5.77	5.70	5.76
1600	5.388	5.888	5.555	5.859		5.86		
1700	5.450	5.896	5.598	5.928		5.93		
1800	5.502	5.903	5.636	5.990		6.00		
2000	5.585	5.914	5.695	6.100				6.05
2250	5.661	5.924	5.749	6.217				6.16
2500	5.717	5.931	5.788	6.321				6.26
2750	5.758	5.936	5.818	6.451				6.34
3000	5.790	5.940	5.840	6.503				6.42

a) DeSorbo & Tyler, Ref. 8

b) McDonald, Ref. 7

c) Brickwedde, et al., Ref. 9

d) Wagman, et al., Ref. 10

Lattice Spacing and Thermal Expansion

Because the experimental data were not sufficient to provide a reliable plot of the a-direction thermal expansion coefficient, α_a, versus temperature, Riley was unable to use equation 6a. Riley's results were derived using equation 8a, with the further assumption that the constant C could be neglected.

Kellett and Richards(14) have reported measurements of a-spacing over the temperature range 290 to 3300°K. The author analyzed the combined data of Kellett and Richards and Nelson & Riley(15) by two methods: (1) the data were analyzed directly by use of equation 8a, and (2) the a-spacing versus temperature data were reduced to mean α_a values by the approximation

$$(\alpha_a)_T = \frac{2\,(a_2 - a_1)}{(a_2 + a_1)(T_2 - T_1)}\ , \qquad (10)$$

where a_1 and a_2 are the a-spacings measured at temperatures T_1 and T_2, and the mean temperature, T, equals $(T_2 + T_1)/2$.

Due to the uncertainties associated with the measured a-spacings, additional smoothing of the mean α_a values was necessary to avoid large random variations and to aid in the least-squares analysis, using equation 6a.

The least squares analysis of the a-spacing and mean α_a data, by use of equations 8a and 6a, yielded slightly different values for the coefficients A, B and C; because of the uncertainties associated with the data, this small difference was not unexpected. By variation of the coefficients, within the bonds established from the two methods, the best simultaneous fit to both equations was found to result from the values:

$A = 0.7023 \times 10^{-6}$ moles/cal
$B = -0.4337 \times 10^{-6}$ moles/cal
$C = -0.830 \times 10^{-10}$ deg^{-2}
$a_o = 2.46168$ Å

Figure 1 shows the fit of equation 8a to the measured a-spacing data and Figure 2 compares the smoothed α_a data with the results calculated by use of equation 6a and the coefficients listed above. Figure 2 also includes direct α_a measurements recently reported by Bailey and Yates(16).

The theoretical α_a curve departs from the data of Bailey and Yates in a rather marked way below about 250°K; although this departure occurs at a temperature about 100°K higher than that at which the specific heat transition becomes noticeable, perhaps both phenomena stem from the same cause. Riley's results predict slightly more negative values for α_a at temperatures below about 250°C and slightly more positive values above 250°K; however, the differences are so small as to make Riley's curves practically indistinguishable from the present results below about 1000°K. At higher temperatures, Riley's curves of α_a and a-spacing increase more rapidly than do the present results and tend to predict values which lie above Kellett and Richards data. It must be admitted that the differences are not large, for example, Riley's results yield an increase of 0.235% in a-spacing between 300° and 3000°K, while the results reported herein (and, of course the measurements of Kellett & Richards) yield an increase of 0.215%.

Kellett and Richards reported(14) that they followed Riley's procedure to fit the theoretical equations to their data; however, it is obvious that the coefficients which they report do not fit their data and do not correspond to the curves shown in their article.

A similar procedure was used to analyze the c-spacing data of Nelson & Riley(15), Yang(17), Kellett, et. al.(18), and Baskin and Meyer(19). The best simultaneous fit to the c-spacing and mean α_c data was obtained with the coefficients:

$$L = -3.320 \times 10^{-6} \text{ moles/cal.}$$

$$M = 6.512 \times 10^{-6} \text{ moles/cal.}$$

$$N = 0.7187 \times 10^{-8} \text{ deg}^{-2}$$

$$c_o = 6.6818 \text{ Å}$$

Figure 3 shows the fit of the c-spacings, calculated from equation 8b, to the measured values and Figure 4 compares the smoothed α_c data with the results calculated by use of equation 6b and the coefficients listed above. The recent direct measurements of α_c, reported by Bailey and Yates(16), are included on Figure 4. Two points are especially worth noting in regard to Figure 4: (1) although the "best curve" intersects the measurements of Bailey and Yates at about 300°K, it falls below their data at all lower temperatures; and (2) whereas the data of Nelson and Riley show a plateau in the curve of α_c versus temperature, the present results indicate an actual reduction in α_c over the temperature range 500° to 800°K. The length change data reported by Entwisle(20) tend to support this behavior; however, the variation of α_c in this temperature range needs additional investigation.

Riley's theoretical curve of α_c versus temperature lies slightly lower than the present results up to 1200° and, of course, follows the data of Nelson and Riley more closely than do these results; at temperatures above 1200°K, however, it increases much too rapidly, reaching a value of 48×10^{-6} deg^{-1} at 3000°K.

Elastic Moduli and Compressibilities

Riley has shown that the lattice elastic moduli can be calculated by combining equations 7 with the equations for the volumetric (K) and linear compressibilities (K_a and K_c), parallel and transverse to the crystal basal planes:

$$K_a = s_{11} + s_{12} + s_{13} \tag{11a}$$

$$K_c = 2s_{13} + s_{33} \tag{11b}$$

$$K = 2K_a + K_c = 2(s_{11} + s_{12}) + 4s_{13} + s_{33} \tag{11c}$$

It is then easily shown that the elastic moduli can be obtained from the relationships:

$$(s_{11} + s_{12}) = AK/2(A + L + X) \qquad (12a)$$

$$s_{13} = LK/4(A + L + X) \qquad (12b)$$

$$s_{33} = XK/(A + L + X) \qquad (12c)$$

where $X = ML/4B$

In Table 2, the calculated elastic moduli and compressibilities are compared with the "best values" obtained by Spence(21) from a review of previous data, and by Seldin(22) from a review of recent measurements on stress-annealed pyrolytic graphite.

DISCUSSION AND CONCLUSIONS

The very close agreement of the derived values for $(s_{11} + s_{12})$, s_{13} and K_a, with the values given by Spence is somewhat fortuitous, since the derived moduli are dependent on the value assumed for K.

This is more clearly shown in Table 3, where the ratios of the elastic moduli to the volumetric compressibilities are listed. The agreement with the previous evaluations is considered excellent and lends strong support to the validity of using Riley's theoretical equations to analyze available lattice expansion data and to describe the crystal expansion as a function of temperature, as is reported herein.

Using a different approach, Kelly and Walker(24) have recently extended the theory of Komatsu and Nagamiya(25,26) so as to derive a model of the thermal expansion of a graphite crystal, and have obtained an excellent fit of their theoretical equations to the α_c data of Bailey and Yates. At higher temperatures, however, their theoretical equations predict too small an increase of α_c with temperature.

TABLE 2

Elastic Moduli and Compressibilities of a Graphite Single Crystal

(in units of 10^{-13} cm^2/dyne)

Quantity	This Paper(a)	Spence(21)	Seldin(22)	Other
$(s_{11}+s_{12})$	1.05	1.06	0.82±0.07	
s_{13}	-2.49	-2.49	-0.33±0.08	
s_{33}	37.4	33.2	27.5±1.0	
K_a	-1.44	-1.43	+0.49±0.07	
K_c	32.4	28.2	26.8±1.0	28.6(b)
K	-a-	26.3	27.8±1.0	29.6(c)

a) Using K = 29.6 x 10^{-13} cm^2/dyne

b) Measured by Kabalkina and Vereshchagin(23)

c) Recomputed by Gschneidner(11) from the measurements of Bridgman.(12)

TABLE 3

Ratios of Elastic Moduli to Volumetric Compressibility

Quantity	This Paper	Spence(21)	Seldin(22)
$\frac{s_{11}+s_{12}}{K}$	0.036	0.040	0.029
$\frac{s_{13}}{K}$	-0.084	-0.095	-0.012
$\frac{s_{33}}{K}$	1.27	1.26	0.99

It should be noted that a best-fit of equation 6b to only the data of Bailey and Yates would yield a curve of α_c versus temperature quite similar to the "probable best curve" shown as Figure 7 of Reference 24; it is apparent, however, that such large values of α_c could not be reconciled with the measured increase of c-spacing with temperature.

Kelly and Walker(24) have also noted that their results would support a ratio of s_{13}/s_{33} = -0.066 as compared to the ratio - 0.075 obtained from the review by Spence(21) or -0.012 from the review by Seldin(22); the results reported herein yield a ratio s_{13}/s_{33} = B/M = - 0.0666.

The equations describing the lattice expansions and thermal expansion coefficients, reported herein, are believed to be reasonable representations of the behavior of crystallites in nuclear grade graphites over the temperature range 300° to 3000°K.

REFERENCES

(1) Riley, D. P., Proc. Phys. Soc. (London), 57 486 (1945).

(2) Gruneisen, E. and Goens, E., Z. Phys. 29, 141 (1924).

(3) Beattie, J. A., J. Math. Phys., 6, 1 (1920).

(4) Magnus, A., Ann. Phys., 70, 303 (1923).

(5) Newell, G. F., J. Chem. Phys., 23, 2431 (1955).

(6) Komatsu, K., J. Phys. Chem. Solids, 25, 707 (1964).

(7) McDonald, R. A., J. Chem. Eng. Data, 10, 243 (1965).

(8) DeSorbo, W., and Tyler, W. W., J. Chem. Phys., 21, 1660 (1953).

(9) Brickwedde, F. G., et al, J. Res. N.B.S.,37, 263 (1946).

(10) Wagman, D. D., et al, J. Res. N.B.S., 34, 143 (1945), and: Rossini, F. D., et al, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press, Pittsburgh (1953).

(11) Gschneidner, K. A., Jr., in "Solid State Physics", Vol. 16, Academic Press, New York (1965).

(12) Bridgman, P. W., Daedalus, 76, 9 (1945).

(13) Kessom, P. H., and Van der Hoeven, B. J. C., Jr., Phys. Rev., 130, 1318 (1963).

(14) Kellett, E. A. and Richards, B. P., J. Nucl. Mater. 12, 184 (1964).

(15) Nelson, J. B. and Riley, D. P. Proc. Phys. Soc. (London), 57, 477 (1945).

(16) Bailey, A. C. and Yates, B., J. Applied Phys., 41, 5088 (1970).

(17) Yang, K. T., in "Proc. Fifth Conference on Carbon, Vol. 2", Pergamon Press, London (1962).

(18) Kellett,E. A., Jackets, B. P., Richards, B. P., Carbon, 2, 175 (1964).

(19) Baskin, Y. and Meyer, L., Phys. Rev., 100, 544 (1955).

(20) Entwisle, F., Phys. Letters, 2, 236 (1962).

(21) Spence, G. B., in "Proc. Fifth Conference on Carbon, Vol. 2", Pergamon Press, London, (1962).

(22) Seldin, E. J. in "Summary of Papers - Ninth Biennial Conference on Carbon", The Defense Ceramic Information Center, Columbus, Ohio, (1969).

(23) Kabalkina, S. S. and Vereshchagin, L. F., translated in Soviet Physics "Doklady", 5, 373 (1960).

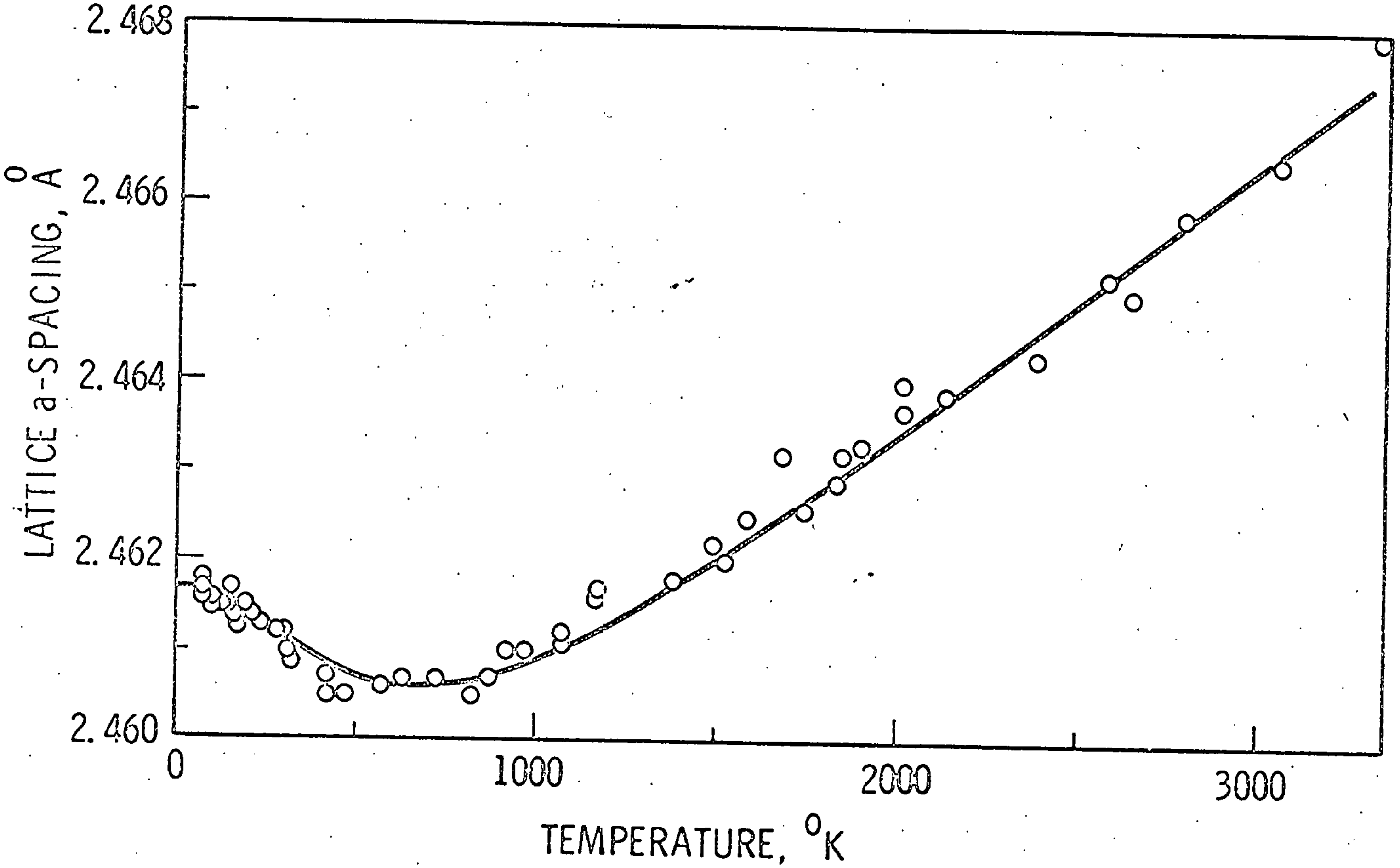
(24) Kelly, B. T. and Walker, P. L., Jr., Carbon, 8, 211 (1970).

(25) Nagamiya, T. and Komatsu, K., J. Chem. Phys., 22, 1457 (1954).

(26) Komatsu, K., J. Phys. Soc. Japan, 10, 345 (1955).

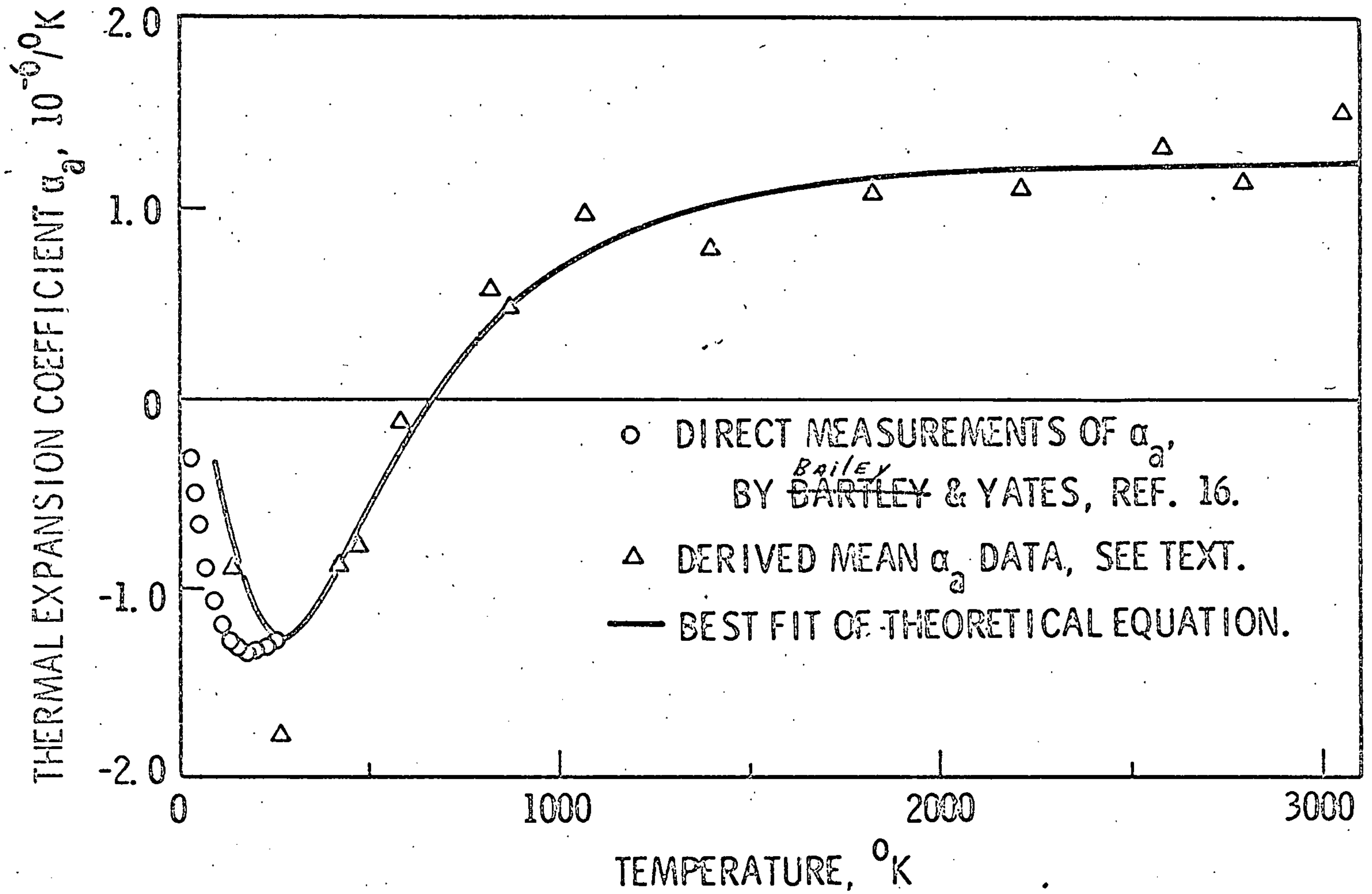
List of Figures

Figure 1



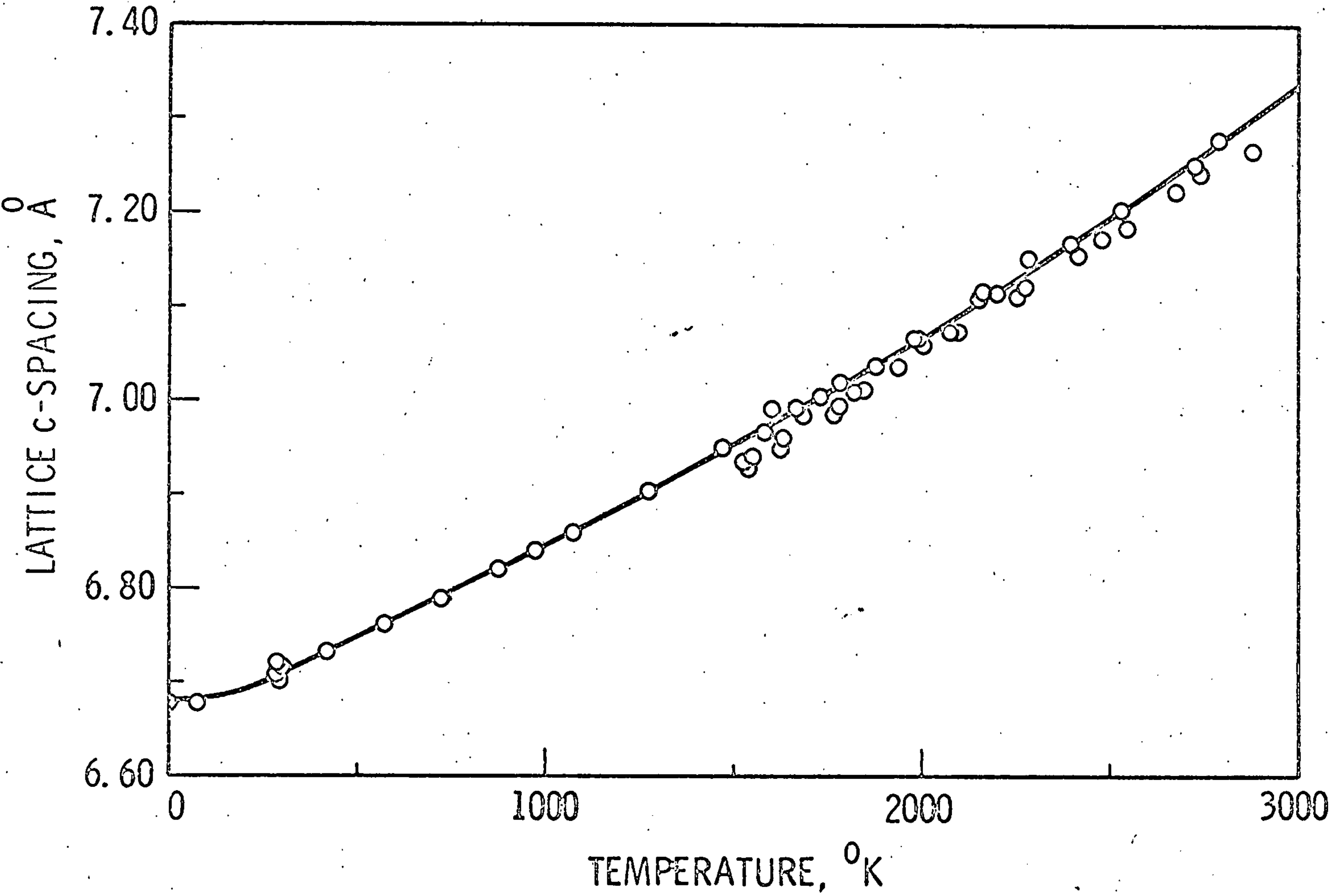
2.468
2.466
2.464
2.462
2.460
LATTICE a-SPACING, Å
0
1000
2000
3000
TEMPERATURE, °K

Figure 2



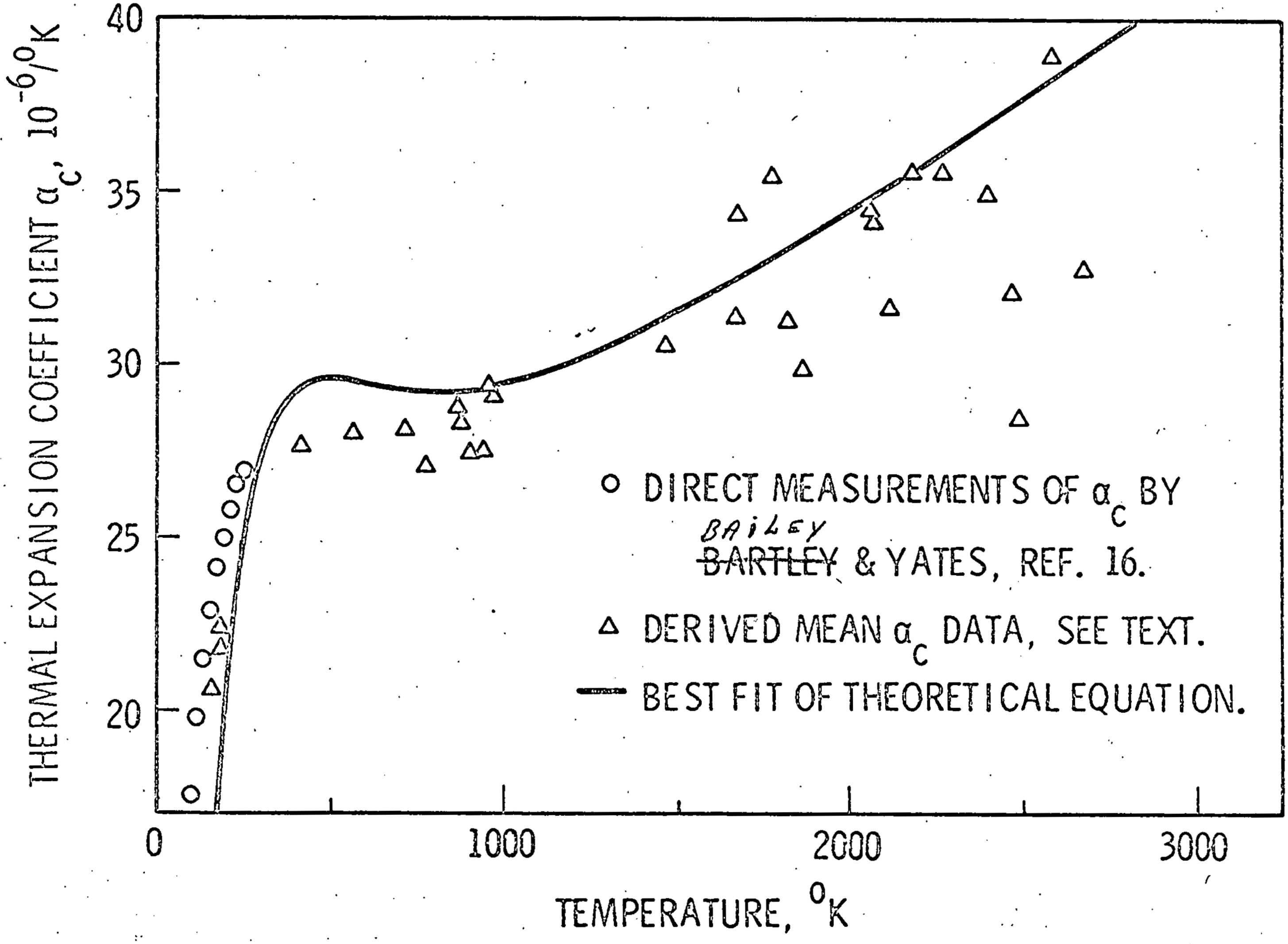
THERMAL EXPANSION COEFFICIENT α_a, 10^{-6}/°K
2.0
1.0
0
-1.0
-2.0
0
1000
2000
3000
TEMPERATURE, °K
○ DIRECT MEASUREMENTS OF α_a,
BY Bailey ~~BARTLEY~~ & YATES, REF. 16.
△ DERIVED MEAN α_a DATA, SEE TEXT.
— BEST FIT OF THEORETICAL EQUATION.

Figure 3



7.40
7.20
7.00
6.80
6.60
LATTICE c-SPACING, Å
0
1000
2000
3000
TEMPERATURE, °K

Figure 4


THERMAL EXPANSION COEFFICIENT α_c, $10^{-6}/^{0}K$
40
35
30
25
20
0
1000
2000
3000
TEMPERATURE, ^{0}K
○ DIRECT MEASUREMENTS OF α_c BY BAILEY ~~BARTLEY~~ & YATES, REF. 16.
△ DERIVED MEAN α_c DATA, SEE TEXT.
— BEST FIT OF THEORETICAL EQUATION.