Recommended Values for the Thermal Expansivity of Silicon from 0 to 1000 K

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Silicon, a high melting point, low expansivity, cubic material which can be obtained readily in high purity form, provides an excellent thermal expansion standard. Various absolute determinations of the thermal expansivity of both single crystal and polycrystalline silicon are used to establish a smooth relationship from 90 to 850 K which is believed to be reliable to roughly 10^{-8} K^{-1}, and which is extrapolated to 1000 K. Values also are suggested for temperatures to absolute zero.

Key words: high temperature expansivity; silicon; standard expansivities; thermal expansivity.

1. Summary of Thermal Expansivity Data

The CODATA Task Group on Thermophysical Properties has suggested that compilations be made of "best" or "recommended" values for some thermophysical (and electrical) properties of a few key materials. The present summary of thermal expansivity data for silicon from very low temperatures to roughly 900 K was prepared in response to a request from this Task Group. As G. K. White has pointed out[1,2] silicon is an ideal candidate for a standard reference material for thermal expansion measurements since it is cubic with a high melting point, it can be obtained readily in high purity form, and it has a relatively small expansion coefficient with respect to most materials (at most, one fifth that of copper). Problems which arise when electrical contacts need to be placed on silicon samples have been discussed by Carr *et al.*[3] and by Lyon *et al.*[4]

Because of its low expansivity, the most useful silicon expansivity data for our purposes will be those which have been determined in an absolute, not relative, manner. Lyon *et al.*[4] give a complete discussion of previous data for temperatures below 300 K, as does White[2] for earlier high temperature data. Only more recent data, mostly at high temperature and the most significant earlier data are included below. X-ray measurements (see Batchelder and Simmons[5] for silicon results) satisfy this "absolute" condition, but are not sufficiently sensitive to compete directly with dilatometers which are based on interferometric or parallel plate capacitor techniques.[6] In turn, the sensitivity of most interferometric methods becomes inadequate at low temperatures,[7] where a combination of small expansivities and the need for small absolute temperature increments limits the useable sensitivity. Here, parallel plate capacitor techniques provide perhaps the only practical basis for dilatometry. Carr, McCammon, and White[3] first used an absolute capacitance dilatometer to study the expansivity of silicon, with later work by Ibach[8] who used a different design for work to 300 K. The most accurate capacitance dilatometry on silicon at any temperature has been reported by Lyon *et al.*[4] who used Kroeger's absolute dilatometer[9] to obtain data from 14 to 340 K with a stated accuracy of 10^{-9} K^{-1} in the expansivity or 0.1%, whichever is greater. The absolute interferometric dilatometers of Ibach,[8] Norton *et al.*,[10] Roberts,[11] and Bennett[12] have been used to obtain expansivity data for silicon[8,10,13–15] with some of these data serving as the basis for previous standard expansivity recommendations by White.[2] The small expansivity of silicon makes it unnecessary to distinguish between the thermodynamic definition of the expansivity ($\alpha = (\partial \ln L / \partial T)_p$) and the practical definition $\alpha' = (L_{20})^{-1} (\partial L / \partial T)_p$, where L_{20} is the length of the sample at 20 °C.

The following recommended expansivities for silicon are based almost exclusively on the data of Lyon *et al.*[4] to 340 K and of Roberts[14] from 300 to 850 K, since these are the most extensive and appear to be the most precise both in expectation and in practice, and they are consistent to within estimated accuracy with other absolute data. White[2] had discussed other high temperature data which are, as will be shown below, inconsistent with an extrapolation of the recommended values. The general features of the expansivity relation for silicon are shown in Fig. 1. The scale of the figure is not sufficient to indicate a very small positive expansivity below 18 K,[4] although the negative expansivity between 18 K and roughly 120 K is clearly evident. Smith and White[16]

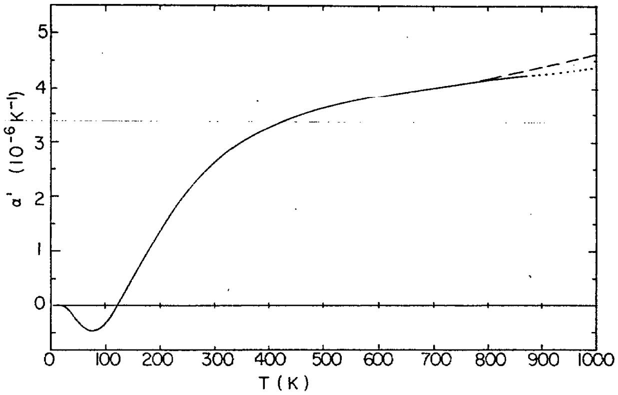

FIGURE. 1. The temperature dependence of the thermal expansivity of silicon. A region of small positive expansivity below 18 K (Ref. 4) cannot be resolved in this figure. The dotted line above 850 K represents an extrapolation of Eq. (1), while the dashed line is that recommended by White (Ref. 2).

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TABLE. 1. Coefficients which when used with Eq. (1) generate the smooth (90 to 850 K) expansivity relation.

$a = -0.687\times10^{-6}\ \mathrm{K}^{-1}$
$A = 5.000\times10^{-6}\ \mathrm{K}^{-1}$
$\theta_E = 685\ \mathrm{K}$
$B = 0.220\times10^{-6}\ \mathrm{K}^{-1}$
$b = 0.316$
$\Phi_0 = 395\ \mathrm{K}$

discuss this general behavior as characteristic of tetrahedrally bonded solids. Lyon *et al.*[4] analyzed their results in terms of power series fits to the data in three overlapping regions, and used these to calculate a table of smooth values. Roberts[14] fitted an eighth-order power series to a combination of the results of Lyon *et al.*[4] (90 to 340 K) and his own (300 to 850 K), and found systematic deviations at low temperatures and possibly at high temperatures. Since power series representations may not be suitable for extrapolation, an alternative procedure is to use the close relationship between the heat capacity and the thermal expansivity to provide a first-order representation, with an essentially ad hoc additive correction term used to provide a "true" representation. We have chosen to use the following expression to represent the expansivity of silicon from 90 to 850 K,

$$\alpha'_{\mathrm{SM}} = (L_{20})^{-1}\left(\frac{\partial L}{\partial T}\right)_p$$

$$= a + A\frac{x^2 e^x}{(e^x-1)^2} + B\frac{(y-1)^2}{1+by}, \qquad (1)$$

where the first function corresponds to the heat capacity in the Einstein model, with $x = \theta_E/T$ ($\theta_E = 685$ K is close to the Debye temperature for silicon), and the second function corresponds to a small deviation which is roughly symmetrical about the temperature $\Phi_0 = 395$ K ($y = T/\Phi_0$) and which contributes 20% to the calculated α' at 80 K and 4.3% at 850 K. The first derivative of each of these terms varies smoothly and slowly with temperature at high temperature, so perhaps it is reasonable to expect that this relation can be used for extrapolation to high temperatures. This need not be the case for a power series representation.

Table 1 contains the parameters for Eq. (1) which can be used to reproduce to within roughly $10^{-8}\ \mathrm{K}^{-1}$ the data of Lyon *et al.*[4] from 80 to 340 K and those of Roberts[14] from 300 to 850 K. Figure 2 shows the deviations of these data from this relation. The scatter of Roberts' results suggests an accuracy of from $0.005\times10^{-6}\ \mathrm{K}^{-1}$ to $0.01\times10^{-6}\ \mathrm{K}^{-1}$ (from 0.2% to 0.4%), while the Lyon *et al.*[4] data are smooth to roughly $0.002\times10^{-6}\ \mathrm{K}^{-1}$. Other results, which show more scatter and are less accurate, are indicated in Fig. 3. These include those of Carr *et al.*,[3] Ibach[8] (capacitance for 300 K and below, interferometric for higher temperatures), and Bennett.[15] The dashed curve is the cubic relation which Bennett[15] used to represent his data. Roberts[17] recently has extended his measurements down to 80 K, with substantial loss in the absolute accuracy of the expansivities below 150 K due to the smaller magnitudes. He concludes that his "results strongly support the findings of Lyon *et al.*[4] from 150 to 280 K." The scatter of his data about the Lyon *et al.*[4] smooth relation in this temperature region is similar to that shown for high temperatures in Fig. 2.

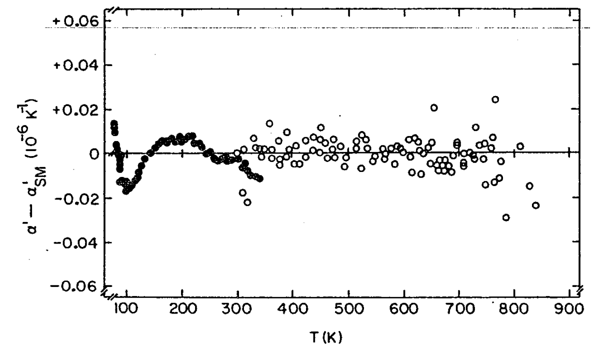

FIGURE. 2. Differences above 90 K between the actual data of Lyon *et al.* (Ref. 4) (●) and Roberts (Ref. 14) (○) and the expansivities given by Eq. (1) and the parameters in Table 1.

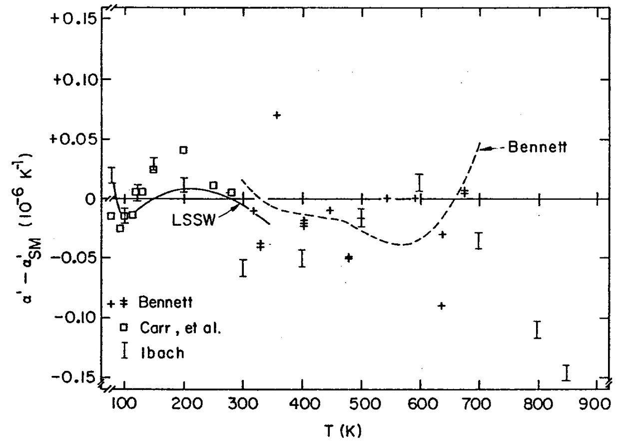

FIGURE. 3. Differences between the actual data of Carr *et al.* (Ref. 3), Ibach (Ref. 8), and Bennett (Ref. 15) (two different runs) and the present smooth relation (as in Fig. 2). The smooth relations of Lyon *et al.* (Ref. 4) (LSSW) and Bennett (Ref. 15) are given also for reference.

The scale of Fig. 2 has been expanded for the 280 to 350 K region in Fig. 4 so that the results of Norton *et al.*[10] can be presented also. These are perhaps the most accurate interferometric data which have been published, and have a stated accuracy of $\pm 0.01\times10^{-6}\ \mathrm{K}^{-1}$ over a temperature range which is limited by technical considerations. Within these limits, these data are consistent with the smooth relation and

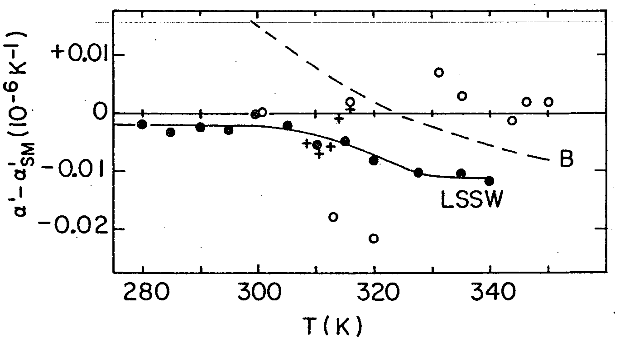

FIGURE. 4. An expanded version of Fig. 2 onto which the data of Norton *et al.* (Ref. 10) (+) have been added. The labeling is the same as in Figs. 2 and 3.

TABLE 2. Recommended values for the expansivity, $\alpha' = (L_{20})^{-1}(\partial l/\partial T)_P$ and for the relative length changes from 20 °C, $\Delta L/L_{20} = [L(T) - L(20\,°\mathrm{C})]/L(20\,°\mathrm{C})$.

T (K)	α'^{a} (10^{-6} K^{-1})	$\Delta L/L_{20}{}^{\mathrm{b}}$ (10^{-6})	T (K)	α'^{a} (10^{-6} K^{-1})	$\Delta L/L_{20}{}^{\mathrm{b}}$ (10^{-6})
0	0.0	−215.5	100	−0.339	−240.1
2	+0.000004	−215.5	120	−0.057	−244.4
4	0.000031	−215.5	140	+0.306	−241.9
6	0.000104	−215.5	160	0.689	−232.0
8	0.00025	−215.5	180	1.061	−214.5
10	0.00048	−215.5	200	1.406	−189.7
12	0.00083	−215.5	220	1.715	−158.5
14	0.00133	−215.5	240	1.986	−121.4
16	0.00111	−215.5	260	2.223	− 79.3
18	−0.00014	−215.5	280	2.432	− 32.8
20	−0.0029	−215.5	293.15	2.555	0
22	−0.0076	−215.5	300	2.618	+ 17.7
24	−0.0147	−215.6	325	2.816	85.7
26	−0.0244	−215.6	350	2.984	158.3
28	−0.0372	−215.7	375	3.128	234.7
30	−0.0529	−215.7	400	3.251	315.
35	−0.103	−216.1	450	3.453	482.
40	−0.164	−216.8	500	3.610	659.
45	−0.229	−217.8	550	3.737	843.
50	−0.293	−219.1	600	3.844	1033.
55	−0.351	−220.7	650	3.935	1227.
60	−0.400	−222.6	700	4.017	1426.
65	−0.438	−224.7	750	4.091	1629.
70	−0.462	−226.9	800	4.159	1835.
75	−0.473	−229.3	850	4.225	2045. ± 4
80	−0.472	−231.6	900	(4.29)	(2257)
85	−0.457	−234.0	950	(4.35)	(2473)
90	−0.429	−236.2	1000	(4.41)	(2692)(± 10)

[a] From Eq. (1) for $T > 300$ K, from Lyon *et al.* (Ref. 4) for $T \leqslant 300$ K. Below 14 K, $\alpha' = 4.8 \times 10^{-13}\, T^3$ K^{-1}.

[b] From an integration of Eq. (1) for $T > 300$ K, from Lyon *et al.* (Ref. 4) for $T \leqslant 300$ K.

with the capacitance dilatometer results of Lyon *et al.*[4] which have a stated accuracy of $\pm 0.003 \times 10^{-6}$ K^{-1} at these temperatures.

The smooth relation [Eq. (1) and Table 1] represents the data of Lyon *et al.* below 300 K and those of Roberts[14] at higher temperatures, and provides a smooth interpolation between these. The agreement in the overlap region (315 to 340 K) is barely satisfactory (Figs. 2 and 4) and suggests the need for additional, independent absolute data. Figure 2 suggests that the accuracy to which Eq. (1) can be used is approximately $\pm 0.01 \times 10^{-6}$ K^{-1} due to the scatter of Roberts' data at high temperatures and the systematic deviations of the Lyon *et al.*[4] data at low temperatures. The occurrence of first minimum and then maximum differences at the lower temperatures perhaps is not surprising, and could be due to different temperatures for the inflection points of the data and of the smooth relation. The actual results of Lyon *et al.*[4] should be used if the highest accuracy is required below 300 K.

The dotted line in Fig. 1 gives the extrapolation of Eq. (1) to 1000 K, and, for comparison, the recommended values of White[2] which are based on results of Zhdanova *et al.*[18] The contribution of the second term in Eq. (1) is 6.5% at 1000 K, to be compared with 4.3% at 850 K, so the extrapolated 1000 K expansivity perhaps could be accurate to 1% or 2%.

Table 2 gives recommended values for the expansivity α' of silicon from 0 to 300 K as given by Lyon *et al.*,[4] and from 300 to 1000 K as calculated from Eq. (1) and the parameters in Table 1. The estimated accuracy varies from that stated by Lyon *et al.*,[4] $\pm 0.1\%$ or $\pm 10^{-9}$ K^{-1}, whichever is greater, below 300 to $\pm 10^{-8}$ K^{-1} at temperatures to 850 K. The expansivities for temperatures greater than 850 K (in parentheses) are extrapolated. Equation (1) can be integrated to give the relative length changes, $\Delta L/L_{20} = (L(T) - L(20\,°\mathrm{C}))/L(20\,°\mathrm{C})$, which are given in Table 2 for temperatures above 300 K, together with the values of Lyon *et al.*[4] for 300 K and below. As Lyon *et al.*[4] state, these relative length changes for temperatures below 300 K are consistent with the x-ray results of Batchelder and Simmons[5] to within the scatter of their data (roughly $\pm 3 \times 10^{-6}$). The small magnitudes of these length changes (0.27% to 1000 K, −0.02% to 10 K) justify our neglect of the difference betwen α and α'.

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