

Reference materials for thermal expansion: certified or not?

Guy K. White

CSIRO Division of Applied Physics, National Measurement Laboratory, Lindfield, NSW 2070, Australia

Keywords: thermal expansion, reference materials.

ABSTRACT

Many dilatometers in common use can have significant systematic errors in determining linear thermal expansion as evidenced by round-robin measurements on reproducible materials. The need for reference materials to check these dilatometers can usually be met by rods of OFHC Cu, semi-conductor grade Si, W, Pt (rather expensive!), sapphire (of specified orientation) etc. which are readily available and for which there are now reliable data.

For legal reasons there may be a need to use certified materials made from a batch which has been measured in a national laboratory. For some years the NBS (now NIST) supplied Cu (SRM 736), sapphire (SRM 732) and W (SRM 737) which are no longer available. Presently available are SRM 731 (borosilicate glass for 80–680 K), SRM 738 (AISI 446 stainless steel for 293–780 K) and SRM 739 (fused silica for 80–1000 K). With some further measurements as a check, MgO and Mo could also be useful reference materials up to high temperatures.

INTRODUCTION

Those who are familiar with experimental data and round-robin measurements of thermal properties will be aware of the errors that can arise because of heat leaks, difficulties in controlling or measuring the temperature, etc. Thermal expansion is no exception in this regard.

The AGARD study of alumina, copper, platinum, tungsten and gold (Fitzer and Weisenburger, 1972) illustrates differences that occur in data even from experienced laboratories. This emphasizes the need for suitable reference

materials and for agreement on the expansion values associated with them. There may also be a statutory legal need for particular samples of material to be measured and certified in an accredited national laboratory, such as Standard Reference Material (SRM) from NIST (formerly NBS) in the USA.

The first such standard from NBS was copper SRM 736 certified in 1969 (Hahn 1970) and revised in 1975. Later certificates from NBS were for fused silica SRM 739 in 1971 (Hahn and Kirby, 1972a), borosilicate glass SRM 731 in 1972 (see Hahn and Kirby, 1974), tungsten SRM 737 in 1976 (Kirby and Hahn, 1976), sapphire SRM 732 in 1977 (Hahn, 1978) and stainless steel SRM 738 (AISI 446) in 1986 (Hahn, 1986). Of these borosilicate glass, fused silica and stainless steel are listed in the current NIST Catalogue. Fortunately the other materials—copper, tungsten and sapphire—are available commercially in sufficiently high state of purity to be very useful as ‘standards’ for calibrating or checking dilatometers. I shall discuss these below and some other suitable solids such as Si, Mo and Pt.

Firstly consider the basic mechanisms of thermal expansion which explain why thermal expansion, like heat capacity, is generally insensitive to small changes in chemical or physical purity. For example various copper samples with impurity levels of 0.1, 0.01 or 0.001% have expansion coefficients which are not measurably different except at very low temperatures, below 20 K. Whether they are strained or annealed makes little difference. Only in some magnetic materials such as Invar or low-expansion glasses do small changes in purity affect the expansion behavior at normal temperatures. Why is this so? Thermal expansion (or contraction) is controlled by the internal (thermal) pressure produced in the solid when the temperature is changed and by the compressibility of the solid. The amount of internal pressure depends on the temperature and volume derivatives of the free energy. The compressibility modulus is not sensitive to trace impurities and the free energy is only altered measurably at low temperature by specific impurities, e.g. Fe or Mn in Cu (see review by Barron et al., 1980).

Although chemical and physical impurities generally exert only a secondary influence on the internal energy and thermal expansion, it is still desirable to choose reference materials which are available in a well characterized state of high purity (say, > 99.95%), are stable and are isotropic. Two commonly used reference materials, vitreous silica and sapphire, fail to meet the respective conditions of stability and isotropy but have been chosen because of other desirable features.

The other reference materials, Cu, Si, W, Pt and Mo are all isotropic, cover a wide range of temperatures and expansivity (see Fig. 1).

Note that values $\alpha^* = (1/\ell_{293})(d\ell/dT)$ are given here and *not* the thermodynamic quantity $\alpha = (1/\ell_T)(d\ell/dT)$. A fuller treatment of this topic will be

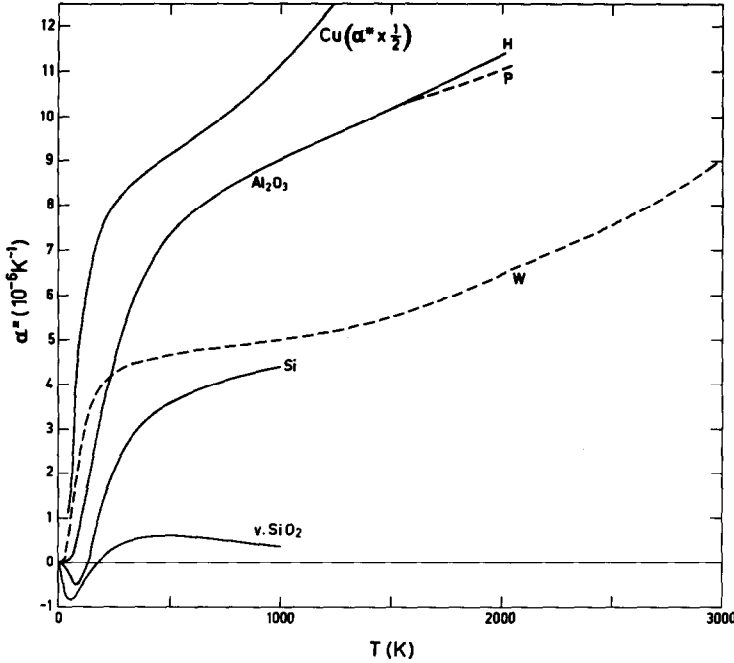


Fig. 1. Linear expansivity α^* of some reference solids (Swenson et al. 1985).

published shortly in a CINDAS volume on thermal expansion of solids, edited by R.E. Taylor. Also CODATA Bulletin No. 59 has a chapter (Swenson et al., 1985) giving recommended values of thermal expansion for Cu, Si, W and Al_2O_3 .

ALUMINA ($\alpha\text{-Al}_2\text{O}_3$)

Alpha-alumina is readily available as a polycrystalline ceramic or in single crystal form as sapphire. It is stable up to the melting temperature near 2300 K. Crystals are of hexagonal structure and therefore anisotropic with the principal coefficient of linear expansion parallel to the symmetry axis, α_{\parallel} , being about 12% larger above room temperature than that normal to the axis, α_{\perp} .

At an arbitrary angle ψ , $\alpha_{\psi} = \alpha_{\perp} \sin^2 \psi + \alpha_{\parallel} \cos^2 \psi = \alpha_{\perp} + (\alpha_{\parallel} - \alpha_{\perp}) \cos^2 \psi$.

The volume coefficient, $\beta = 2\alpha_{\perp} + \alpha_{\parallel}$ and the average linear coefficient α_{av} is $\beta/3$ equalling α_{ψ} when $\psi = 55^\circ$.

White and Roberts (1983) analyzed selected data on single and polycrystalline material from nine reference sources. They adjusted the values obtained on single crystals at angles of 58° and 59° to a common angle of

TABLE 1

Recommended values for $\alpha - Al_2O_3$ (Swenson et al. 1985).

| T (K) | α_{\parallel}^* $10^{-6}/K$ | α_{\perp}^* $10^{-6}/K$ | α_{av}^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} | T (K) | α_{av}^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} |
|----------|---------------------------------------|-----------------------------------|--------------------------------|---------------------------------|----------|--------------------------------|---------------------------------|
| 20 | 0.006 | 0.003 | 0.004 | -635 | 1100 | 9.34 | 6485 |
| 30 | 0.022 | 0.013 | 0.016 | -635 | 1200 | 9.59 | 7430 |
| 40 | 0.054 | 0.039 | 0.044 | -635 | 1300 | 9.85 | 8400 |
| 50 | 0.120 | 0.08 | 0.095 | -634 | 1400 | 10.31 | 9400 |
| 60 | 0.22 | 0.16 | 0.18 | -633 | 1500 | 10.31 | 10420 |
| 70 | 0.35 | 0.26 | 0.29 | -631 | 1600 | 10.51 | 11460 |
| 80 | 0.53 | 0.40 | 0.44 | -627 | 1700 | 10.67 | 12520 |
| 90 | 0.73 | 0.57 | 0.61 | -622 | 1800 | 10.84 | 13600 |
| 100 | 0.98 | 0.73 | 0.81 | -615 | 1900 | 11.05 | 14690 |
| 120 | 1.52 | 1.15 | 1.28 | -595 | 2000 | 11.37 | 15810 |
| 140 | 2.14 | 1.64 | 1.80 | -565 | | | |
| 160 | 2.72 | 2.15 | 2.34 | -524 | | | |
| 180 | 3.30 | 2.70 | 2.90 | -473 | | | |
| 200 | 3.84 | 3.21 | 3.42 | -410 | | | |
| 250 | 5.01 | 4.27 | 4.52 | -212 | | | |
| 293 | 5.80 | 5.06 | 5.30 | 0 | | | |
| 300 | 5.90 | 5.15 | 5.40 | 37 | | | |
| 350 | 6.50 | 5.77 | 6.08 | 324 | | | |
| 400 | 7.08 | 6.36 | 6.64 | 642 | | | |
| 450 | 7.57 | 6.81 | 7.10 | 986 | | | |
| 500 | 7.94 | 7.19 | 7.46 | 1350 | | | |
| 550 | 8.30 | 7.50 | 7.75 | 1730 | | | |
| 600 | 8.55 | 7.72 | 7.99 | 2125 | | | |
| 650 | 8.79 | 7.93 | 8.18 | 2530 | | | |
| 700 | 8.97 | 8.10 | 8.35 | 2940 | | | |
| 800 | 9.29 | 8.36 | 8.62 | 3790 | | | |
| 900 | 9.54 | 8.65 | 8.86 | 4665 | | | |
| 1000 | 9.70 | 8.83 | 9.09 | 5560 | | | |

55° and averaged these with data on polycrystalline alumina to obtain the values in Table 1. Above 1100 K, there was only one report of data in both principal directions so that only α_{av}^* is given in the Table above 1000 K. White and Roberts fitted a 5th order polynomial from 300 to 2000 K and plotted deviations of individual values of α_{av}^* . As shown in Fig. 2, these amount to $\sim 1\%$ or $0.1 \times 10^{-6} K^{-1}$ near 1000 K.

The polynomial for use above 300 K is:

$$\alpha^*(10^{-6} K^{-1}) = -3.262 + 46.706t - 76.714t^2 + 64.4455t^3 - 26.1987t^4 + 4.1154t^5$$

where $t = T/1000$.

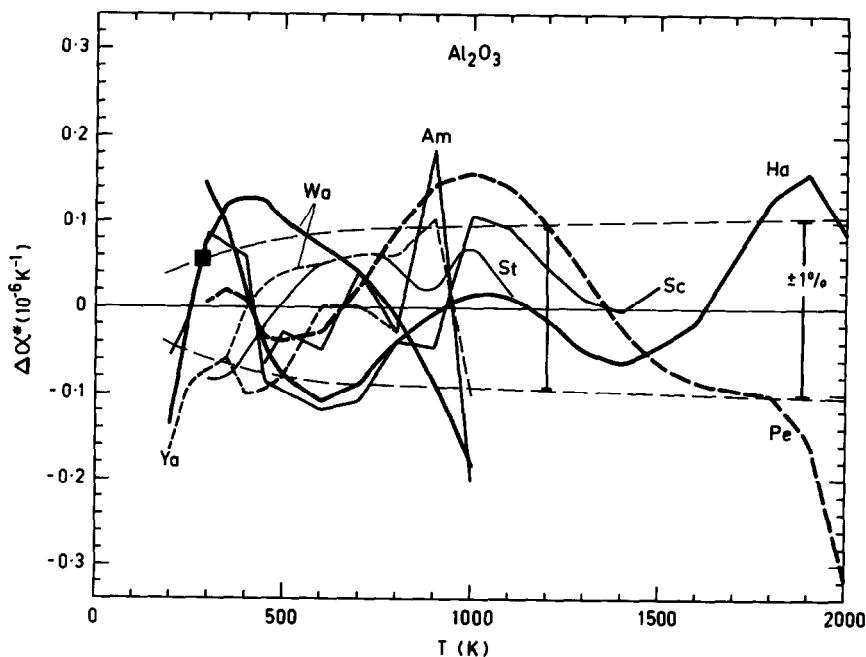


Fig. 2. α -Alumina. Deviation plot of average values of α^* (White and Roberts 1983).

The values in Table 1 were also used in the CODATA Bulletin 59 referred to above. The data of Hahn (1978) were obtained on three samples of sapphire as the basis of the NBS Certificate for SRM 732.

BOROSILICATE GLASS

In 1972 six rods from a batch of borosilicate glass containing 70% SiO_2 , 17% B_2O_3 , 8% K_2O , 3% Al_2O_3 , and 1% each of Na_2O and Li_2O were measured at the NBS in a Fizeau interferometer (Hahn and Kirby, 1974) in the range 80 to 680 K. The rods had been annealed at 789 K and cooled slowly to 523 K. With a least-square fit to a 5th order polynomial, they obtained values of α and $\Delta l/l$ with a stated uncertainty of $\pm 0.03 \times 10^{-6} \text{K}^{-1}$ in α . This constitutes SRM 731 (Table 2).

A problem with silicate glasses as reference materials is that their thermal expansion may vary considerably with composition, particularly with the amount of 'network filler' (e.g. K_2O , Na_2O) so that it cannot be inferred that borosilicate glass from sources other than the SRM 731 will have the same values of α even though the compositions appear to be approximately the same.

TABLE 2

Certificate values for SRM 731-borosilicate glass (Hahn and Kirby 1974).

| T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} | T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} |
|----------|---------------------------|---------------------------------|----------|---------------------------|---------------------------------|
| 80 | | -819 | 293 | 4.78 | 0 |
| 90 | | -797 | 300 | 4.82 | 34 |
| 100 | 2.64 | -771 | 320 | 4.91 | 131 |
| 110 | 2.86 | -744 | 340 | 4.99 | 230 |
| 120 | 3.07 | -714 | 360 | 5.06 | 330 |
| 130 | 3.25 | -683 | 380 | 5.11 | 432 |
| 140 | 3.43 | -649 | 400 | 5.15 | 535 |
| 150 | 3.58 | -614 | 420 | 5.19 | 638 |
| 160 | 3.72 | -578 | 440 | 5.21 | 742 |
| 170 | 3.85 | -540 | 460 | 5.23 | 847 |
| 180 | 3.97 | -501 | 480 | 5.25 | 952 |
| 190 | 4.08 | -460 | 500 | 5.26 | 1057 |
| 200 | 4.17 | -419 | 520 | 5.26 | 1162 |
| 210 | 4.26 | -377 | 540 | 5.27 | 1267 |
| 220 | 4.34 | -334 | 560 | 5.27 | 1372 |
| 230 | 4.41 | -290 | 580 | 5.27 | 1478 |
| 240 | 4.48 | -246 | 600 | 5.27 | 1583 |
| 250 | 4.54 | -201 | 620 | 5.28 | 1689 |
| 260 | 4.60 | -155 | 640 | 5.29 | 1794 |
| 270 | 4.66 | -109 | 660 | | 1900 |

COPPER

Copper is readily obtained in high state of purity, e.g. OFHC copper at 99.98+% and ultra-pure at 99.9999%. Comparative measurements on various coppers including 99.9999%, electrolytic tough-pitch, deformed and annealed, etc. indicated differences in α were less than 1% above 30 K (e.g. White 1972).

The first expansion SRM (No. 736) from the NBS in 1969 was based on interferometric measurements of five samples of 99.99% from 20 to 800 K with stated inaccuracy in α of less than $0.05 \times 10^{-6} K^{-1}$ (Hahn, 1970). Later the data were re-analyzed, partly as a result of measurements on similar material at Oak Ridge (Kollie et al., 1974) to give slightly larger values of α (Kirby and Hahn, 1975). These and 12 other selected sets of data were the basis of an evaluation by White and Roberts (1980) as part of the CODATA 'key values' project. The resulting recommended values are reproduced in Table 3 and can be represented from 300 to 1250 K by the polynomial:

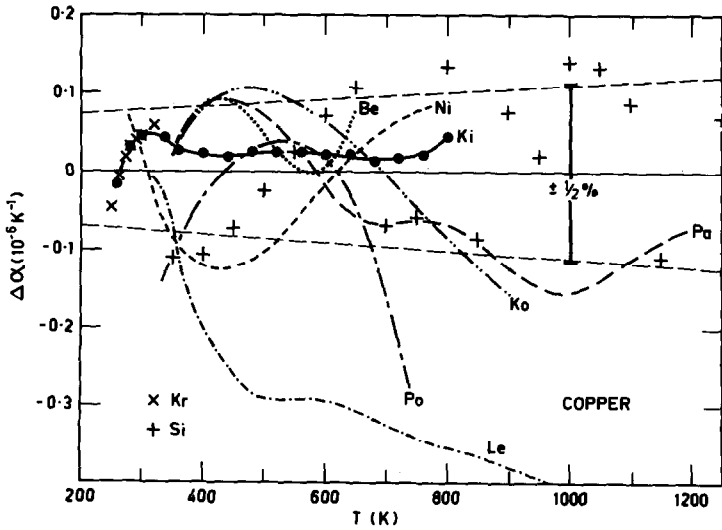
$$\alpha^*(10^{-6}K^{-1}) = 11.1113 + 33.360t - 74.022t^2 + 99.728t^3 - 64.930t^4 + 17.015t^5$$

where $t = T/1000$.

TABLE 3

Recommended values for copper (Swenson et al. 1985).

| T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} | T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} |
|----------|---------------------------|---------------------------------|----------|---------------------------|---------------------------------|
| 10 | 0.030 | -3257 | 140 | 13.19 | -2349 |
| 12 | 0.052 | -3257 | 160 | 14.03 | -2077 |
| 14 | 0.083 | -3257 | 180 | 14.67 | -1789 |
| 16 | 0.126 | -3257 | 200 | 15.19 | -1491 |
| 18 | 0.186 | -3256 | 250 | 16.11 | -706 |
| 20 | 0.263 | -3256 | 293.15 | 16.65 | 0 |
| 25 | 0.56 | -3254 | 300 | 16.70 | 114 |
| 30 | 1.00 | -3250 | 350 | 17.12 | 959 |
| 35 | 1.58 | -3244 | 400 | 17.51 | 1824 |
| 40 | 2.27 | -3234 | 500 | 18.23 | 3611 |
| 50 | 3.84 | -3204 | 600 | 18.93 | 5469 |
| 60 | 5.46 | -3157 | 700 | 19.67 | 7398 |
| 70 | 6.98 | -3095 | 800 | 20.46 | 9404 |
| 80 | 8.33 | -3018 | 900 | 21.32 | 11490 |
| 90 | 9.49 | -2929 | 1000 | 22.26 | 13670 |
| 100 | 10.49 | -2829 | 1100 | 23.31 | 15950 |
| 120 | 12.05 | -2602 | 1200 | 24.58 | 18340 |

Fig. 3. Copper. Deviation of α^* from polynomial fit (Swenson et al. 1985).

Below 300 K, the tabulated values are from Kroeger and Swenson (1977) who give fitting polynomials in their report for ranges 20–55, 45–110 and 90–325 K. Deviations of the data above 300 K from the polynomial are in Fig. 3 and reach about $0.1 \times 10^{-6} K^{-1}$ ($\sim 0.5\%$) at 1000 K.

PLATINUM

Platinum has been used as a thermal expansion reference material and associated temperature measurement standard in X-ray diffraction (e.g. see Simmons, 1970). Campbell (1967) tabulates the expansion at 2 deg. intervals from 0°C to 1700°C in "The Handbook of X-Rays". However platinum has not been widely used as a reference material in dilatometry for the obvious reason of expense.

Following earlier interferometry measurements at the NBS (e.g. Hahn and Kirby, 1972b) and The Institute of Metrology in Leningrad (Amatumi et al., 1976), a detailed study was reported by Edsinger et al. (1986) resulting from the NBS gas thermometer project. Kirby (1991) has analyzed much of these data to produce polynomial fits and a table of smoothed values. There is a paucity of experimental values below 300 K. Kirby did not use the data of Nix and MacNair (1942) but interpolated between 85 and 283 K using the ratio of α/C (where C = heat capacity) as a guide as this ratio should be nearly constant over this range.

SILICA (VITREOUS)

Vitreous silica is used widely as a reference material because it has a small value of α at normal and elevated temperatures, e.g. $\alpha \sim 0.4 \times 10^{-6} K^{-1}$ at 293 K and many push-rod dilatometers are made of it. Vitreous silica is produced either by fusing the mineral quartz or by hydrolysis of silicon tetrachloride. The word 'quartz' should be reserved for the crystalline form of hexagonal symmetry and not confused with the fused or vitreous material as their properties are very different.

The expansion coefficient of fused or vitreous silica varies with method of preparation, particularly heat treatment so that α at 293 K ranges from about 0.3×10^{-6} (for silica aged at 1400°C and cooled) to about $0.5 \times 10^{-6} K^{-1}$ (for silica with a fictive temperature of 1000°C). The latent instability has obvious disadvantages for precision dilatometry and makes it necessary that the reference material should be of well defined thermal history or be certified by an appropriate laboratory and not be heated for any appreciable time above 1000 K. The other drawback of silica at low temperatures (e.g. $T < 100$ K), is that α becomes negative and large in magnitude compared with many ceramics. This variability is well illustrated in Fig. 4 (Hahn and Kirby, 1972a).

The NBS produced SRM 739 in 1971 as a result of interferometric measurements on five samples of fused silica which had been annealed as follows: heated to 1100°C at 200°C/h, held at 1100°C for seven hours, cooled to

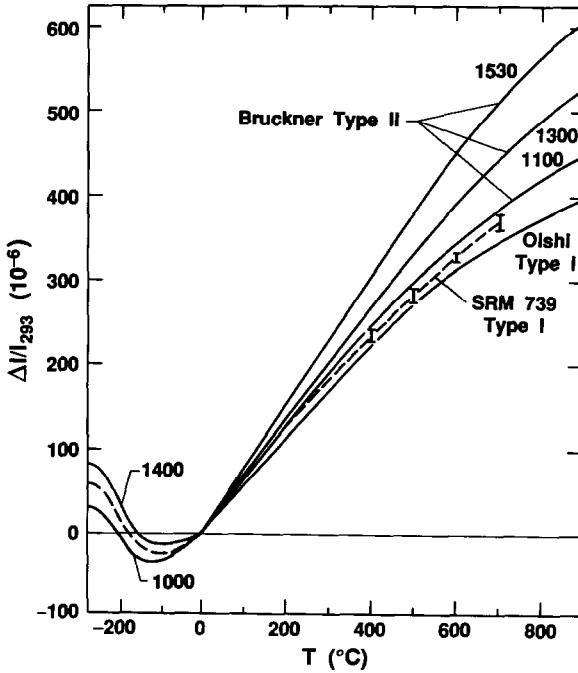


Fig. 4. Vitreous Silica. Variation of expansion with thermal aging (Hahn and Kirby 1972).

900°C at 12°C/h and cooled to room temperature (Hahn and Kirby, 1972a). They stated the uncertainties in α to be $\pm 0.03 \times 10^{-6} K^{-1}$. The values in the Certificate are given in abbreviated form in Table 4 down to 80 K. The bracketed values below 80 K are an approximation based on the data from 2–100 K for five samples aged at 1000°C, 1050°C and 1400°C (White and Birch, 1965).

SILICON

Silicon is an isotropic material with a small expansion coefficient ($\alpha = 2.55 \times 10^{-6} K^{-1}$ at 293 K) and readily available in ultra-pure condition as a result of the needs of the semiconductor industry. Si can also be obtained as a dislocation-free single crystal of such physical and chemical purity that it is used as a standard of lattice spacing and density. Therefore it is surprising that it has not been more widely favored as a reference material for expansion.

During the 1970s, cooperative and accurate measurements of linear expansion near room temperature were made at University of Arizona, Corning (N.Y.), Iowa State University and CSIRO/NML (Sydney) as well as

TABLE 4

Certificate values for SRM 739-vitreous silica (extrapolation in brackets).

| T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} | T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} |
|----------|---------------------------|---------------------------------|----------|---------------------------|---------------------------------|
| 10 | (-0.22) | (47) | 293 | 0.48 | 0 |
| 20 | (-0.58) | (43) | 300 | 0.49 | 3.5 |
| 30 | (-0.75) | (36.5) | 320 | 0.53 | 13.5 |
| 40 | (-0.80) | (29) | 340 | 0.56 | 24.5 |
| 50 | (-0.80) | (21.5) | 360 | 0.58 | 36 |
| 60 | (-0.78) | (14) | 380 | 0.60 | 47.5 |
| 70 | (-0.73) | (7) | 400 | 0.61 | 59.5 |
| 80 | -0.70 | -1 | 450 | 0.63 | 91 |
| 90 | -0.61 | -7.5 | 500 | 0.63 | 122 |
| 100 | -0.53 | -13 | 550 | 0.61 | 153 |
| 120 | -0.38 | -22.5 | 600 | 0.59 | 183 |
| 140 | -0.24 | -28.5 | 650 | 0.55 | 212 |
| 160 | -0.10 | -32 | 700 | 0.53 | 238 |
| 180 | 0.02 | -32.5 | 750 | 0.49 | 264 |
| 200 | 0.13 | -31 | 800 | 0.47 | 288 |
| 220 | 0.23 | -27.5 | 850 | 0.44 | 311 |
| 240 | 0.32 | -22 | 900 | 0.41 | 332 |
| 260 | 0.39 | -14.5 | 950 | 0.38 | 352 |
| 280 | 0.45 | -6 | 1000 | 0.37 | 371 |

at NPL(Teddington) which confirmed that α for various samples of semiconductor grade Si, polycrystalline and single crystal agreed within $0.01 \times 10^{-6} K^{-1}$ (in range 280–420 K). Some of these measurements extended down to 4.2 K and up to 800 K. Swenson (1983), with the encouragement of the CODATA Task Group on Thermophysical Properties, made a critical evaluation of these data and produced ‘recommended values’ for the CODATA Bulletin 59. More recently the shortage of precision data above 700 or 800 K was met by measurements at the NRLM (Tsukuba, Japan) (Okaji, 1988) and Swenson (1990) has re-evaluated the data fitting them to the reference function (90–1300 K):

$$\alpha^*(\text{in } 10^{-6} K^{-1}) = -0.713 + 5.04x^2 e^x / (e^x - 1)^2 + 0.180(y - 1)^2 / (1 + 0.36y)$$

where $x = 685/T$ and $y = T/435$.

The smoothed values of α^* and expansion are shown in Table 5 and deviations of the selected data are shown in Fig. 5. Maximum probable errors in $10^6 \alpha^*$ are estimated to be 0.001 below 20 K, 0.02 from 40 to 600 K and 0.05 from 600–1200 K.

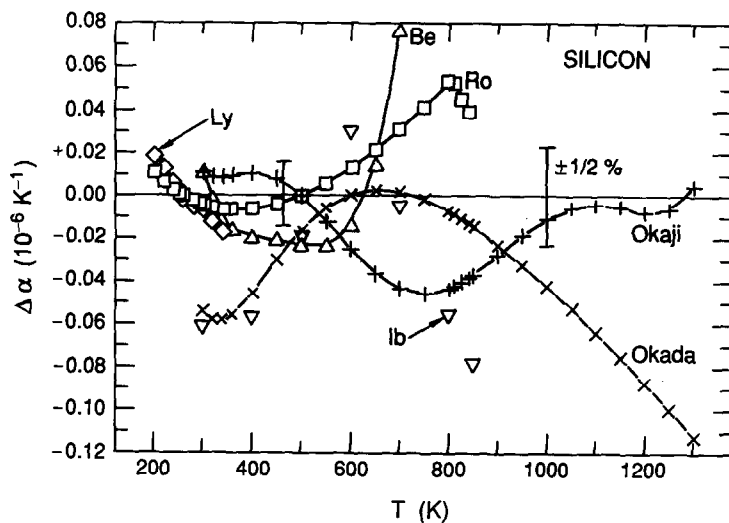


Fig. 5. Silicon. Deviation of α^* values from smooth fit (Swenson 1990).

TABLE 5

Linear thermal expansion of silicon (Swenson 1990).

| T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} | T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} |
|----------|---------------------------|---------------------------------|----------|---------------------------|---------------------------------|
| 10 | 0.0005 | -215.5 | 160 | 0.69 | -232 |
| 12 | 0.0008 | -215.5 | 180 | 1.06 | -214.5 |
| 14 | 0.0013 | -215.5 | 200 | 1.40 | -189.5 |
| 16 | 0.0011 | -215.5 | 250 | 2.10 | -101 |
| 18 | -0.0001 | -215.5 | 293.15 | 2.56 | 0 |
| 20 | -0.003 | -215.5 | 300 | 2.62 | 18.0 |
| 25 | -0.019 | -216 | 350 | 2.99 | 158.5 |
| 30 | -0.053 | -216 | 400 | 3.26 | 315 |
| 35 | -0.103 | -216 | 500 | 3.61 | 660 |
| 40 | -0.164 | -217 | 600 | 3.83 | 1033 |
| 50 | -0.29 | -219 | 700 | 4.00 | 1424 |
| 60 | -0.40 | -223 | 800 | 4.11 | 1829 |
| 70 | -0.46 | -227 | 900 | 4.21 | 2244 |
| 80 | -0.47 | -232 | 1000 | 4.30 | 2670 |
| 90 | -0.43 | -236 | 1100 | 4.39 | 3105 |
| 100 | -0.34 | -240 | 1200 | 4.47 | 3547 |
| 120 | -0.06 | -244.5 | 1300 | 4.56 | 3999 |
| 140 | 0.31 | -242 | | | |

STAINLESS STEEL (AISI 446)

This is a high-chromium steel containing approximately 24.1% Cr, 0.58% Si, 0.31% Mn, 0.29% Ni, 0.09% C and remainder Fe which was measured at NBS by Hahn (1986) from 293 to 980 K in a Fizeau interferometer. The expansivities listed in Table 6 are stated in the Certificate to have "... a precision of $0.03 \times 10^{-6} K^{-1}$... and are made on two specimens taken from widely spaced positions in the stock of material ...". The Certificate also notes that "... if this SRM is heated above 780 K the resulting annealing will cause shrinkage of about 115×10^{-6} and a permanent change in expansivity ..." although values given for the annealed material show α to be changed by only about half a percent. Note that available data for Ni/Cr steels such as AISI 304, 310 and 316 are very different from this Cr stainless steel e.g. $\alpha \sim 16 \times 10^{-6}$ at room temperature for the 18:8 steels (e.g. see Touloukian et al., 1975).

TABLE 6

Certificate values for SRM 738-AISI 446 stainless steel (Hahn 1986).

| T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} | Uncertainty in $\Delta l/l_{293}$ 10^{-6} |
|----------|---------------------------|---------------------------------|--|
| 293 | 9.76 | 0 | |
| 300 | 9.81 | 69 | 2 |
| 340 | 10.04 | 466 | 8 |
| 380 | 10.28 | 872 | 14 |
| 420 | 10.52 | 1288 | 18 |
| 460 | 10.76 | 1714 | 22 |
| 500 | 11.00 | 2149 | 26 |
| 540 | 11.23 | 2593 | 29 |
| 580 | 11.47 | 3048 | 32 |
| 620 | 11.71 | 3511 | 34 |
| 660 | 11.95 | 3984 | 36 |
| 700 | 12.19 | 4467 | 36 |
| 740 | 12.42 | 4959 | 37 |
| 780 | 12.66 | 5461 | 37 |

TUNGSTEN

Tungsten is a body-centered cubic metal with high melting point ($T_m = 3693 K$) and relatively small expansion coefficient: $\alpha = 4.4 \times 10^{-6} K^{-1}$ at 293 K. As a potential reference material Kirby (1972) measured the linear expansion of two sintered rods and one arc-cast rod from 293 to 1800 K.

TABLE 7

Recommended values for tungsten (Roberts 1990).

| T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} | T (K) | α^* $10^{-6}/K$ | $\Delta l/l_{293}$ 10^{-6} |
|----------|---------------------------|---------------------------------|----------|---------------------------|---------------------------------|
| 10 | 0.006 | -876 | 600 | 4.74 | 1410 |
| 15 | 0.019 | -876 | 700 | 4.82 | 1890 |
| 20 | 0.048 | -876 | 800 | 4.89 | 2375 |
| 25 | 0.102 | -875 | 900 | 4.97 | 2865 |
| 30 | 0.20 | -875 | 1000 | 5.05 | 3365 |
| 40 | 0.53 | -871 | 1100 | 5.13 | 3870 |
| 50 | 0.96 | -864 | 1200 | 5.22 | 4390 |
| 60 | 1.43 | -852 | 1300 | 5.32 | 4910 |
| 70 | 1.88 | -835 | 1400 | 5.43 | 5450 |
| 80 | 2.30 | -814 | 1500 | 5.55 | 6000 |
| 90 | 2.61 | -790 | 1600 | 5.68 | 6570 |
| 100 | 2.88 | -762 | 1700 | 5.83 | 7160 |
| 120 | 3.30 | -700 | 1800 | 5.98 | 7760 |
| 140 | 3.59 | -631 | 2000 | 6.32 | 9020 |
| 160 | 3.81 | -557 | 2200 | 6.72 | 10360 |
| 180 | 3.97 | -479 | 2400 | 7.18 | 11780 |
| 200 | 4.10 | -398 | 2600 | 7.71 | 13280 |
| 250 | 4.30 | -188 | 2800 | 8.34 | 14890 |
| 293.15 | 4.42 | 0 | 3000 | 9.12 | 16620 |
| 300 | 4.43 | 31 | 3200 | 10.09 | 18520 |
| 350 | 4.48 | 254 | 3400 | 11.33 | 20680 |
| 400 | 4.55 | 479 | 3500 | 12.07 | |
| 500 | 4.65 | 940 | | | |

Later Kirby and Hahn (1976) measured six samples from a sintered compact (density 19.23 g/cm³ and purity > 99.96%) as the basis for SRM 737. In the Certificate they state "... this SRM 737 should not be heated above 700 K in air. Vacuum or dry non-oxidizing atmospheres (helium, argon) ... should be used ... to higher temperatures".

For the CODATA project on key values, White and Roberts (1983) fitted a 5th order polynomial from 250 to 3400 K to the values from NBS and six other sources. Below 300 K data were insufficient for fitting and those chosen for CODATA were from Kirby and Hahn (1976) from 80–300 K and from White et al. (1978) below 80 K. The specimens used were generally sintered rods except 'C' of Kirby which was arc-cast.

Recently Müller and Cezairlyan (1990) have used their sub-second transient technique for interferometric measurement of expansion of tungsten using a tube cut from the sintered SRM 737, over the range 1500 to 3600 K. Roberts (1990) has included these data in a re-fitted polynomial for the range 300–

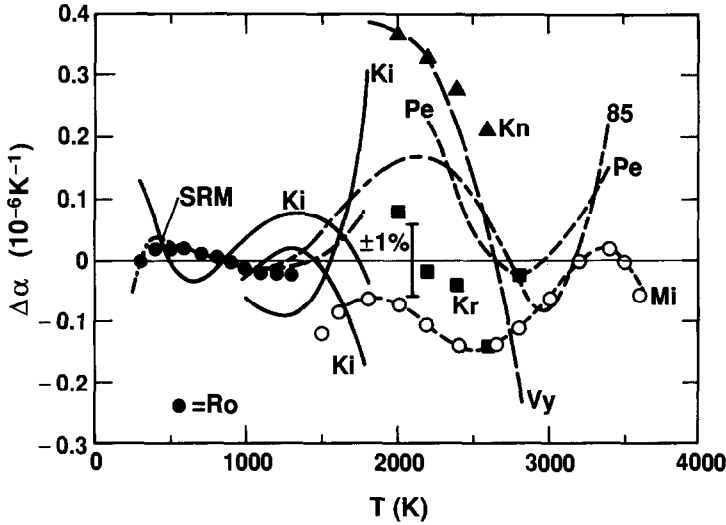


Fig. 6. Tungsten. Deviation of α^* values from smooth fit (White and Roberts 1983).

3500 K:

$$\alpha^*(10^{-6} K^{-1}) = 3.873 + 2.562t - 2.8613t^2 + 1.9862t^3 - 0.58608t^4 + 0.071586t^5$$

where $t = T/1000$. Values in Table 7 are from this equation above 300 K and from the CODATA Bulletin (Swenson et al., 1985) below 300 K. Deviations are in Fig. 6.

OTHER REFERENCE MATERIALS

Two materials which are suitable by reason of isotropy, purity, availability and temperature range are molybdenum and magnesium oxide but each needs further accurate data for verification.

Magnesium Oxide

MgO has a cubic rock-salt structure, melts at about 3100 K and has a linear coefficient $\alpha = 10.4 \times 10^{-6} K^{-1}$ at 293 K. It is readily available in sufficiently pure state to be a useful reference material up to at least 2500 K but needs more accurate data to verify the expansion, particularly above 1300 K. It was the subject of an inter-laboratory comparison involving 29 investigators under the auspices of the US Bureau of Mines (Campbell, 1962). Campbell derived smoothed values for the lattice expansion $\Delta a/a$ and recommended these for use as an internal standard in X-ray diffraction (Campbell, 1967).

However the primary data were of rather mixed accuracy and appear to lead to unreliable values at the higher temperatures (Simmons, 1970). Recently Anderson and Zou (1990) have evaluated thermodynamic functions for MgO from 300 to 2000 K including α values based on Suzuki (1975) who measured the expansion from 300 to 1273 K and extrapolated above this. Their values of α agree within $0.1 \times 10^{-6} K^{-1}$ ($\sim 1\%$) with the tabulation of Kirby et al. (1972) in the AIP Handbook.

Molybdenum

Molybdenum like tungsten is a stable body-centered cubic metal with a high melting temperature ($T_m = 2897$ K) and linear coefficient $\alpha = 5.1 \times 10^{-6} K^{-1}$ at 293 K. Many of the measurements of expansion are listed by Toloukian and Ho (1975) and in an analysis of the heat capacity by Choudbury and Brooks (1984). Of particular note are the sub-second measurements at NBS on SRM 781 (heat capacity and enthalpy standard) by Müller and Cezairlyan (1985) from 1500 to 2800 K and those at the High Temperature Institute in Moscow (e.g. Amatumi et al. 1976). The latter were done on various samples, sintered, arc-melted, and single crystals as basis for a reference standard. Amatumi et al. used a silica dilatometer from 373 to 1173 K and an optical comparator from 2073 to 2823 K. The NBS and Russian values of expansion appear to be in agreement, differing by less than 2% over the 1500–2800 K range. From 100 to 1000 K there are not many data at the 0.05×10^{-6} level of accuracy in α which obtains for tungsten. There is a clear need for further careful study of this material.

Graphite (POCI-AXM 5Q1)

Graphite in single crystal form is highly anisotropic, the atoms forming a layered structure with strong co-valent bonding in the basal plane and weak bonding between planes. Thus the linear coefficient normal to the symmetry axis α_{\perp} is near zero below 1000 K while $\alpha_{\parallel} \sim 30 \times 10^{-6} K^{-1}$ at 1000 K. However polycrystalline fine-grained material has been the subject of many investigations as a prospective reference material for many thermophysical properties at high temperatures. In particular POCO AXM 5Q1 (graphitized at 2500°C by Poco Graphite Inc., Garland, Texas) has been found to give reproducible data despite variations in density. A thermal conductivity SRM 8424/5/6 is now available from NIST (Taylor and Groot, 1980) as a result of tests correlating variations of thermal conductivity with density and electrical resistivity.

Taylor and Groot have measured thermal properties of a number of samples of AXM-5Q1 of density near 1.7 g/cm^3 . They find that the thermal expansion

$\Delta l/l$ could be represented within $\pm 1\%$ from 20 to 2550°C by the polynomial (t in °C):

$$10^2 \Delta l/l = 0.018613 + 0.678978(t/1000) + 0.0163081(t/1000)^2 \\ + 0.110737(t/1000)^3 - 0.050326(t/1000)^4 + 0.0084718(t/1000)^5$$

In the AGARD study (Fitzer and Weisenburger, 1972) various graphites were measured. Gaal (1974) has also given the results of a United States round-robin on POCO graphite which showed reproducibility of $\Delta l/l$ at the $\pm 1\%$ level and agreement between observers at the $\pm 2.5\%$ level. His graphs show mean values of $\Delta l/l$ of about 0.74% at 1000°C and 1.74% at 2000°C which agree reasonably with AGARD and Taylor and Groot.

REFERENCES

- Amatumi, A.N., Malyutina, T.I., Chekhovskoi, V.Y., and Petukhov, V.A. (1976), *High Temp-High Press.*, 8, 565-70
- Anderson, O.L., and Zou, K., (1990), *J. Phys. Chem. Ref. Data*, 19, 69-82
- Barron, T.H.K., Collins, J.G. and White, G.K., (1980), *Adv. Phys.* 29, 609-730
- Campbell, W.J., (1962), *U.S. Bur. Mines Rept. Invest.* 6115
- Campbell, W.J. (1967) in *Handbook of X-Rays* (Ed. E.F. Kaelble, McGraw-Hill New York), Ch. 13
- Choudbury, A. and Brooks, C.R., (1984), *Int. J. Thermophys.* 5, 403-29
- Edsinger, R.E., Reilly, M.L. and Schooley, J.F. (1986), *J. Res. Nat. Bur. Stand.* 91, 333-56
- Fitzer, E. and Weisenburger, S. (1972), *High Temp-High Press.* 4, 559-71
- Gaal, P.S. (1974), in *Thermal Expansion-1973*, 102-16 (Eds. R.E. Taylor and G.L. Denman, Amer. Inst. Phys., New York)
- Hahn, T.A. (1970), *J. Appl. Phys.* 41, 5096-101
- Hahn, T.A., (1972), *SRM 731, NBS Certificate* (Washington DC)
- Hahn, T.A. (1978), *Thermal Expansion* 6, 191-202 (Ed. I.D. Peggs, Plenum Press, New York)
- Hahn, T.A., (1986) *SRM 738, NBS Certificate* (Gaithersburg, Maryland)
- Hahn, T.A. and Kirby, R.K. (1972a) in *Thermal Expansion-1971*, 13-24 (Eds. G.M. Graham and H.E. Hagy, Amer. Inst. Phys., New York)
- Hahn, T.A. and Kirby, R.K. (1972b), in *Thermal Expansion-1971*, 87-95 (Eds. G.M. Graham and H.E. Hagy, Amer. Inst. Phys., New York)

- Hahn, T.A. and Kirby, R.K. (1974), in *Thermal Expansion-1973*, 93–101 (Eds. R.E. Taylor, G.L. Denman, Amer. Inst. Phys. New York)
- Kirby, R.K. (1972), *High Temp-High Press.*, 4, 459–62
- Kirby, R.K. (1991), *Int. J. Thermophys.*, 12, 679–85
- Kirby, R.K. and Hahn, T.A. (1975), *Revised Certificate for SRM 736*, NBS
- Kirby, R.K. and Hahn, T.A. (1976), *SRM 737 Certificate* (Washington DC NBS)
- Kirby, R.K., Hahn, T.A. and Rothrock, R.D. (1972), in *American Inst. of Physics Handbook* 3rd Ed., Ch. 4f
- Kollie, T.G., McElroy, D.L., Hutton, J.T. and Ewing, W.M. (1974), *Thermal Expansion-1973*, 129–46 (Eds. R.E. Taylor and G.L. Denman, Amer. Inst. Phys. New York)
- Kroeger, F.R. and Swenson, C.A. (1977), *J. Appl. Phys.* 48, 853–63
- Miiller, A.P. and Cezairlyan, A. (1990), *Int. J. Thermophys.* 11, 619–28
- Miiller, A.P. and Cezairlyan, A. (1985), *Int. J. Thermophys.* 6, 695–704
- Nix, F.C. and MacNair D., (1942), *Phys. Rev.* 61, 74–8
- Okaji, M. (1988), *Int. J. Thermophys.* 9, 1101–9
- Roberts, R.B. (1990), CSIRO, Sydney, priv. comm.
- Simmons, R.O. (1970), *J. Appl. Phys.* 41, 2235–40
- Suzuki, I. (1975), *J. Phys. Earth*, 23, 145–59
- Swenson, C.A. (1983), *J. Phys. Chem. Ref. Data* 12, 179–82
- Swenson, C.A. (1990), Iowa State Univ., priv. comm.
- Swenson, C.A., Roberts, R.B. and White, G.K. (1985), in *Thermophysical Properties of Some Key Solids*, Ch.4, (Eds. White, G.K. and Mingos, M.L., Oxford Pergamon Press) CODATA Bulletin 59
- Taylor, R.E. and Groot, H. (1980), *High Temp-High Press.* 12, 147–60
- Touloukian, Y.S. Kirby, R.K., Taylor, R.E. and Lee, T.Y.R., (1975), Vol 12 in *Thermophysical Properties of Matter* (Eds., Touloukian Y.S., and Ho, C.Y.), Thermal Expansion: Metallic Elements and Alloys, (Plenum Press, New York)
- White, G.K. (1972), in *Thermal Expansion-1971*, AIP Conf. Proc. No. 3 (Eds. M.G. Graham, H.E. Hagy, AIP, New York), 59–64
- White, G.K. and Birch, J.A. (1965), *Phys. Chem. Glasses* 6, 85–9
- White, G.K. and Roberts, R.B. (1980), *High Temp-High Press.* 12, 311–6
- White, G.K. and Roberts, R.B. (1983), *High Temp-High Press.* 15, 321–8
- White, G.K., Smith, T.F. and Carr, R.H. (1978), *Cryogenics* 18, 301–3