Thermal Expansion of Vitreous Silica at Low Temperatures

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Measurements of the linear expansion coefficient α of pure vitreous silicas and ULE (Corning) silica at liquid-helium temperatures indicate a linear term analogous to that observed in the specific heat of glasses. This term, $\alpha \approx -0.10 \times 10^{-8} T$ K^{-1}, leads to a large Grüneisen parameter γ between -40 and -50, suggestive of a tunneling process.

Anderson, Halperin, and Varma[1] have suggested that tunneling states with a broad distribution of energy splittings might explain the observations of heat capacity C and heat conductivity K for amorphous solids below ca. 2 K.[2,3] Tunneling should give rise to an anomalously large thermal expansion and associated Grüneisen parameter γ.[4,5] Previously I reported γ values for vitreous silica reaching -8 at 3 K[6,7] but was unable to resolve the expansion coefficient with sufficient precision below this. With slight improvements in the sensitivity of measuring length changes and in calibration, I now report expansions between 3 and 1.5 K which lead to γ values reaching -40 or more. These are comparable in magnitude with values found for the impurity dipole component in alkali halides,[8,9] where Li^+ in KCl and OH^- in NaCl gave Schottky anomalies associated with tunneling states and values of $\gamma \approx 300$ and $+40$, respectively, and CN^- in NaCl gave γ which was very large but *negative*.

Present measurements of the linear coefficient α were made in a three-terminal capacitance dilatometer,[10] with an uncertainty at helium temperatures of $\sim 10^{-10}$ K^{-1} arising from the limit of resolution and calibration errors. Specimens included two vitreous silicas from Thermal Syndicate Limited[7]: Spectrosil aged at 1000°C (density $\rho = 2.200$ g cm^{-3}) and Vitreosil aged at 1400°C ($\rho = 2.203$ g cm^{-3}); also two rods of Corning ULE 7971 containing 7–8% TiO_2 for which $\rho = 2.199$ g cm^{-3}. The values of α/T^3 are shown in Fig. 1 and may be compared with C/T^3 for vitreous silica[7] in the lower part of the graph. Between 3 and 7 K, $\alpha \approx bT^3$ whereas $C_p \approx BT^3 + CT^5$. Below 3 K the measurements of C_p extend to 0.8 K and show an additional term: $66 \times 10^{-6} T$ J/g mol K. The α values between 3 and 1.5 K are relatively less precise but indicate a T term for each of the vitreous samples of $-(0.105 \pm 0.015) \times 10^{-8} T$ K^{-1}. We may compare the magnitude of the T terms using $\gamma = 3\alpha V/C_p \chi_s$, where the molar volume V is 22.7

cm^3 and the adiabatic compressibility χ_s is 2.75 $Mbar^{-1}$, and calculate $\gamma = -47 \pm 7$.

Included in Fig. 1 are data for a devitrified material, Zerodur from Schott (Mainz, West Germany), α values being negative and proportional to T^3 between ca. 2 and 10 K. Rather similar values were obtained for Cer-Vit from Owens-Illinois.[11] It is not clear whether any significant departure from T^3 dependence occurs below 3 K in these "ceramics."

There have been comprehensive reports and reviews of the "anomalous" properties of glasses[2,3,12,13] but they have not included recent data on expansion or density effects so I shall summarize the picture as follows.

Firstly for temperature region I: $T < 2$ K.

(a) C_v exhibits a linear term for all glasses.[2,3] The magnitude is rather insensitive to bonding or to additives, e.g., vitreous SiO_2, $SiO_2 + Na_2O$, and B_2O_3 are comparable. There is some evi-
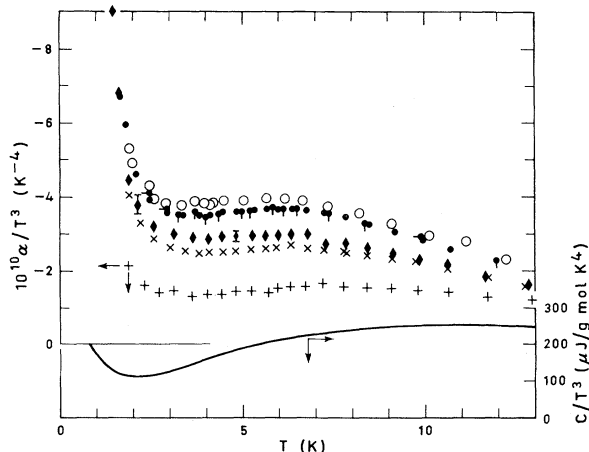

FIG. 1. Plot of α/T^3 versus temperature for vitreous silica (◆, Spectrosil "1000"; ×, Vitreosil "1400"), Corning ULE silica (○, No. 1; ●, No. 2, ●, No. 2, at a later date), and also a ceramic glass (+, Zerodur). Note that all are negative. Lower graph shows C/T^3 for Spectrosil "1400."

dence that an increase in density (by neutron irradiation) increases the T term significantly.[7]

(b) $K \propto T^m$ where $m = 1.8$–1.9 for all glasses[2,3] and the magnitude is fairly insensitive to bonding or additives.

(c) α shows evidence of a negative T term for SiO_2 and $SiO_2 + TiO_2$; therefore γ is negative and $|\gamma| \gtrsim 40$ (cf. the similarly large γ value arising with electric dipoles in alkali halides).

Secondly for temperature region II: ca. 5–15 K.

(a) C_v differs from glass to glass in terms of departure from the Debye model. In tetrahedrally bonded glasses such as SiO_2, C_v exceeds that calculated from elastic data by a factor of 3 or more; this also occurs in cristobalite[12] and at somewhat higher temperatures in all the diamond-structure crystals. Taking the minimum value of Θ_D as an indicator of the departure from the Debye model, one finds that this minimum is reached at ca. $\Theta_D/50$ for vitreous silica compared with $\Theta_D/15$ for Si, Ge, etc.[14] An increase in density resulting from heat treatment or neutron irradiation decreases C_v markedly,[7] i.e., $d\ln C/d\ln V \gtrsim 10$, but network fillers do not have great effect.

(b) K has a plateau for all glasses over this temperature region with a magnitude of 1 mW/cm K (within a factor of 2). In SiO_2, an increase in density from heat treatment or irradiation increases K[15,16]: i.e., $d\ln K/d\ln V \sim 10$. Network fillers have little effect.

(c) α is negative for the tetrahedrally bonded glasses SiO_2 and GeO_2[17] as it is also for the diamond-structure crystals Ge, Si, GaAs, etc.[14] Network fillers such as Na_2O suppress this negative pattern while modifiers like TiO_2 and B_2O_3 do not. A change in density also has an effect: $d\ln\alpha/d\ln V \sim 100$.

For region I, I conclude that the present evidence on thermal expansion of vitreous silica supports the importance of tunneling below 2 or 3 K, but data on α for vitreous Se, B_2O_3, etc., are needed.

For region II, the density dependences of C and K are consistent if it is assumed that some of the local modes which contribute to C also control K by resonant scattering of phonons. The negative expansion seems to arise from acoustic shear modes for which the velocity has a negative pressure dependence. These also cause ultrasonic attenuation and are inhibited by network fillers. It is not clear that the same modes are as dominant in determining α as in C and K.

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