

## Thermal expansion and heat capacity of vitreous B<sub>2</sub>O<sub>3</sub>

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The linear expansion coefficient  $\alpha$  of vitreous B<sub>2</sub>O<sub>3</sub> was measured from 2 to 90 K.  $\alpha(T)$  is negative below 3.3 K but is not fitted uniquely by a simple polynomial. The heat capacity  $C_p$  of the same sample was measured from 2 to 20 K and is consistent with earlier data. For  $T < 3.5$  K,  $C_p = 562T^3 + 44T^5$   $\mu\text{J/mol K}$  giving  $\Theta_0^{\text{el}} = 258.5$  K compared with  $\Theta_0^{\text{el}} = 271$  K. The "anomalous" thermal properties of vitreous solids in the range 2 to 20 K are discussed.

### INTRODUCTION

The thermal and elastic properties of silica and silicate glasses have been of technical interest for a long time.<sup>1</sup> More recently, studies of other glasses at low temperatures have raised a number of fundamental questions.<sup>2-4</sup> Some of the more puzzling properties are the ubiquitous "knee" in the thermal conductivity  $\lambda(T)$  near to 10 K, the enhanced heat capacity  $C$  in that temperature region, the negative thermal expansion in the tetrahedrally bonded glasses, and particularly the temperature dependencies of  $C$  and  $\lambda$  below 1 or 2 K.

The negative values of the coefficient of thermal expansion of vitreous silica below 150 K were attributed by Smyth<sup>1</sup> to the influence of transverse modes of vibration in the open silica network. Anderson and Dienes<sup>5</sup> pointed out the thermodynamic link between the negative values of the volume coefficient  $\beta$  and the decrease or softening under pressure of the bulk and shear moduli. Later measurements of  $\beta$  in other tetrahedrally bonded glasses including GeO<sub>2</sub> and BeF<sub>2</sub> showed somewhat similar patterns of behavior, but a "triangular" glass B<sub>2</sub>O<sub>3</sub> did not show negative values at least down to about 5 K.<sup>6</sup> Kurkjian *et al.*<sup>7</sup> measured the pressure dependence of the elastic moduli of SiO<sub>2</sub>, GeO<sub>2</sub>, etc., and calculated that the low-temperature limit of the elastic value of the Grüneisen parameter,  $\gamma_0^{\text{el}}$ , is negative for these tetrahedral systems:  $\gamma_0^{\text{el}} = -2.15$  for SiO<sub>2</sub>,  $-1.40$  for BeF<sub>2</sub>,  $-0.88$  for GeO<sub>2</sub>; cf. a value of  $+0.28$  for B<sub>2</sub>O<sub>3</sub>. However, the value  $\gamma_0$  (thermal) for SiO<sub>2</sub> determined from the measurement of the linear coefficient  $\alpha$ , the heat capacity per unit volume  $C_p/V$ , and the adiabatic bulk modulus  $B_s$ , using the expression

$$\gamma = \beta B_s V / C_p = 3\alpha B_s V / C_p,$$

is about  $-7$  at liquid-helium temperatures, showing that modes of vibration other than those measured ultrasonically play a major role in the low-temperature thermal properties. This is most evident also in the heat capacity of vitreous SiO<sub>2</sub> which exceeds that predicted from the elastic properties by a factor of 2-3 near 4 K. In SiO<sub>2</sub> below 2 or 3 K, there is evidence of a negative contribution to  $\beta$  which varies roughly as  $T$  (see review<sup>8</sup>).

We attribute this negative term to tunneling states whose existence was postulated first to account for a  $T$  term (i.e., linear term) in the heat capacity of glasses at low tempera-

tures.<sup>9,10</sup> In SiO<sub>2</sub> the ratios of the linear terms observed in  $\beta$  and  $C_p$  lead to a value  $\gamma \approx -20$ .<sup>11,12</sup> Also in the non-tetrahedrally bonded materials polymethylmethacrylate (PMMA) and vitreous As<sub>2</sub>S<sub>3</sub>,  $\alpha$  measured between 2 and 4 K suggest a negative  $T$  term for which  $\gamma \sim -20$ .<sup>11,13</sup> However, other recent measurements below 2 K on these three materials indicate that  $\gamma$  may vary with  $T$  in different ways.<sup>14,15</sup>

For vitreous B<sub>2</sub>O<sub>3</sub>, heat-capacity measurements near 0.1 K have shown a  $T^{1.45}$  term.<sup>16</sup> This has led us to measure the expansion coefficient of B<sub>2</sub>O<sub>3</sub> from 90 K down to about 2 K to see whether  $\alpha(T)$  is negative and if the Grüneisen ratio is unusual. In order to confirm that our sample was similar in thermal behavior to those measured earlier,<sup>8,17</sup> we also measured  $C_p$  over the range from 2 to 20 K.

### EXPERIMENTAL DETAILS

The sample for measurement was a rod 40 mm long by 20 mm diam. It was cast in a thin-walled (0.05 mm) Pt-Au 5 wt.% crucible with a conical hopper top and cylindrical lower section. The mass of the sample was 15.3 g.

"Suprapur" boric oxide was loaded into the crucible, supported in a purified graphite holder, slowly heated during 24 h to 1000 °C under a vacuum of 1 mPa, and held at that temperature and pressure for 4 h. Titanium-gettered argon was admitted to about 30 kPa, the boric oxide slowly cooled during 24 h to 250 °C and held at that temperature for 16 h, then cooled during 20 h to room temperature. The crucible was peeled off in a dry box and the cast rod coated with Apiezon L grease to protect it from moisture. For the expansion measurements the ends of the rod were ground and lapped flat and parallel and the rod mounted in a three-terminal capacitance dilatometer.<sup>18</sup> Expansion measurements were made over the range 1.8 to 90 K and at room temperature. The accuracy of the expansion measurements at the lower temperatures is limited by the sensitivity which is about 1 pm ( $10^{-2}$  Å). At high temperatures the sensitivity is 1% or better.

The heat capacity of the sample from 1.7 to 20 K was determined in an adiabatic calorimeter<sup>19</sup> in which the addenda containing the heater and thermometer contributed 10-40% of the total heat capacity. The accuracy of the heat-capacity determination was 0.5% or better.

## RESULTS

Figure 1 shows measured values of the heat capacity below 5 K, together with earlier data,<sup>17</sup> which agree within their limits of error. For  $T < 3.5$  K,  $C_p$  can be represented by

$$C_p = 562T^3 + 44T^5 \text{ } \mu\text{J/mol K}$$

$$[C_p = 8.08T^3 + 0.632T^5 \text{ } \mu\text{J/g K}] .$$

Taking the density to be 1.82 g/cm<sup>3</sup>, we calculate a limiting value for the Debye temperature ( $\Theta_0$ ) of 258.5 K from the  $T^3$  term, compared with values of about 271 K calculated from the elastic moduli<sup>7</sup> of a well-dried sample. Lasjaunias, Thoulouze, and Pernot<sup>16</sup> found, for their sample between 0.3 and 1.0 K,

$$C_p \approx 0.9T + 8T^3 \text{ } \mu\text{J/g K} ,$$

while Stephens<sup>10</sup> reported

$$C_p = 1.3T + 11T^3 \text{ } \mu\text{J/g K} .$$

As our measurements do not extend below 2 K we cannot determine the presence or absence of a term linear in temperature, due to the dominant  $T^3$  and  $T^5$  terms. There is good agreement between our  $T^3$  term and that of Lasjaunias *et al.*,<sup>16</sup> who found also that their data were fitted better below 0.1 or 0.2 K with the first term  $1.75T^{1.45} \text{ } \mu\text{J/g K}$ .

Values of the expansion coefficient measured between 1.5 and 6 K are plotted in Fig. 2 in the form  $\alpha/T$  and  $\alpha/T^3$  vs  $T^2$ . There is no indication of a satisfactory fit to a simple polynomial nor does a plot of  $\alpha/T^{3/2}$  vs  $T^{3/2}$  yield anything better. The straight lines drawn on Fig. 2 fit the data within the relatively large errors from 1.8 to 3 or 4 K. If the  $T^3$  term from the fit  $10^{10}\alpha = -2.2T^3 + 0.20T^5 \text{ K}^{-1}$  is associated with the  $T^3$  term in heat capacity, their ratio leads to a

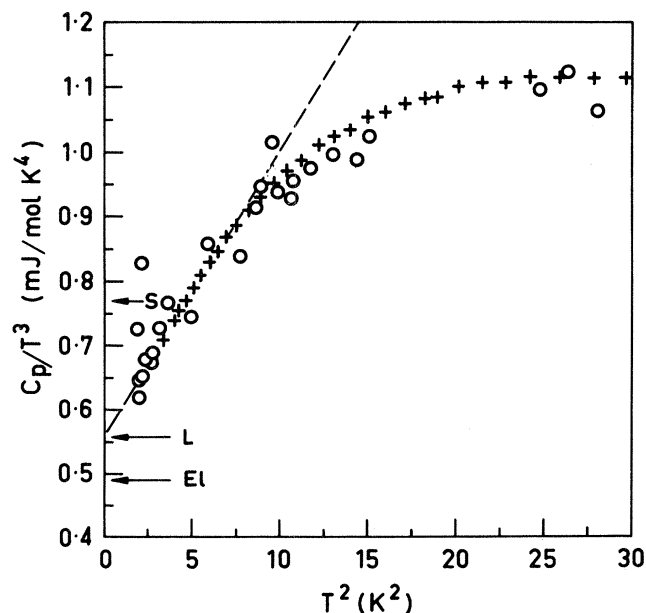


FIG. 1. Heat capacity of vitreous boric oxide below 5 K plotted as  $C_p/T^3$  vs  $T^2$ ; + present, O Jeapes and Leadbetter (Ref. 17). Arrows mark values of the  $T^3$  term measured calorimetrically [ $S$  (Ref. 10),  $L$  (Ref. 16)] and calculated from elastic constants (Ref. 7).

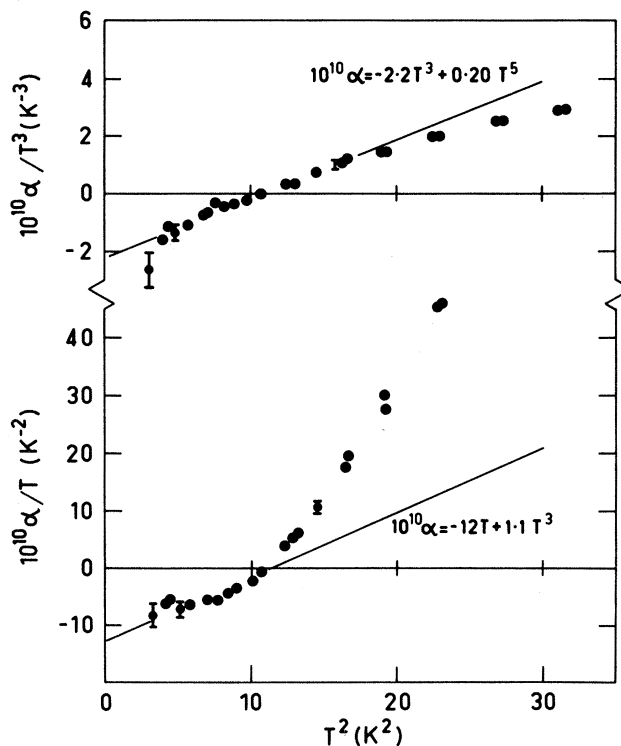


FIG. 2. Values of linear expansion coefficient  $\alpha$  for boric oxide plotted as  $\alpha/T^3$  and  $\alpha/T$  vs  $T^2$ .

TABLE I. Smoothed values for vitreous  $B_2O_3$  of linear expansion coefficient  $\alpha$ , heat capacity  $C_p$ , and Grüneisen parameter  $\gamma = 3\alpha VB_s/C_p$  (using  $B_s = 13$  GPa,  $V = 38.2$  cm<sup>3</sup>).

$T$ (K)	$\alpha$ ( $10^{-8} \text{ K}^{-1}$ )	$C_p$ (J/mol K)	$\gamma$
2	-0.12	0.00590	-0.3
2.5	-0.15	0.0131	-0.2
3	-0.11	0.0252	-0.06
3.5	+0.12	0.0433	+0.04
4	0.65	0.0682	0.14
4.5	1.44	0.100	0.21
5	2.85	0.139	0.31
6	7.1	0.239	0.44
7	13.7	0.365	0.56
8	22.7	0.517	0.65
10	46.2	0.887	0.78
12	76.5	1.31	0.87
14	112	1.82	0.92
16	150	2.34	0.96
18	190	2.88	0.98
20	229	3.42	1.00
25	332	(4.9)	1.00
30	423	(6.6)	0.95
35	513		
40	591		
65	923	(17)	0.81
75	1030	(20)	0.77
85	1110	(23)	0.72
283	1545	(63)	0.36

Grüneisen parameter  $\gamma(T^3) = -0.7$ . On the other hand, the  $T$  term in the alternative "fit,"

$$10^{10}\alpha = -12T + 1.1T^3 \text{ K}^{-1}$$

gives

$$\gamma(T) \sim -25 \text{ and } \gamma(T^3) \sim 0.3$$

assuming

$$C_p = 0.9T + 8.1T^3 + O(T^5) \text{ } \mu\text{J/g K}.$$

The latter value  $\gamma = +0.3$  for the  $T^3$  term is close to the value  $\gamma_0^{\text{el}} = +0.28$  obtained from the pressure dependence of the elastic moduli.<sup>7</sup>

Smoothed values of  $\alpha$  and  $C_p$  are given in Table I together with values of  $\gamma$  calculated assuming that the bulk modulus  $B_s = 13 \text{ GPa}$  (0.13 Mbar) and  $\rho = 1.82 \text{ g cm}^{-3}$ . Bracketed values of  $C_p$  are taken from a graph by Westrum.<sup>20</sup>

### DISCUSSION

The heat capacity of a variety of vitreous materials displays a term  $T^n$  where  $n \approx 1$  which becomes significant below 2 or 3 K and must arise from some excitation with a roughly constant density of states. This is attributed to two-level tunneling states with an energy gap which is randomly distributed over energies equivalent to  $T \leq 1 \text{ K}$ . There is a surprisingly small spread in the magnitude of this term among different vitreous materials.<sup>4,9</sup> As mentioned in the Introduction there is also some evidence for a negative  $T$  term in the expansion coefficient of some glasses.

In the temperature region from  $\sim 2$  to 20 K, the heat capacity and thermal expansion appear to depart from normal but the extent of departure differs considerably from one glass to another. Figure 3 illustrates that the departure of  $C$  from the Debye continuum model is not necessarily a distinguishing feature of the vitreous state. For silica (and also for some sodium silicate glasses<sup>12</sup>) large departures from the Debye background persist to temperatures as low as  $\Theta_D/100$ . But in vitreous  $\text{B}_2\text{O}_3$ ,  $\text{As}_2\text{S}_3$ , and  $\text{GeO}_2$  the "bump" in  $C/T^3$  is less marked and  $C_p$  can be expressed in the form  $AT + BT^3 + CT^5$  at liquid-helium temperatures with a  $T^3$  component which is less than 10% larger than that calculated from elastic data (Figs. 1 and 3).

An increase in the measured  $C$  above that predicted by the Debye continuum model means that there are more modes of vibration excited than are assumed in the model. This may be due to enhanced dispersion in the acoustic spectrum of the solid, or to optic modes of uncertain origin or tunneling states or combinations of all these. Note that a large increase in  $C/T^3$  is observed also in some crystalline materials such as HgTe (Fig. 3) which has the tetrahedrally-bonded zinc-blende structure where some transverse acoustic modes are highly dispersive.<sup>21</sup> Another crystal, alpha-cristobalite, is remarkable for the low reduced temperature at which dispersion effects occur.

The "enhanced" heat capacity in silica and related glasses between 2 and 20 K may be related to "enhanced" negative expansion in this region. As Fig. 4 shows,  $\gamma$  for vitreous silica (and silica containing small amounts of soda) is much more negative than elastic behavior predicts.

We suggest that in vitreous  $\text{SiO}_2$  transverse vibrations of

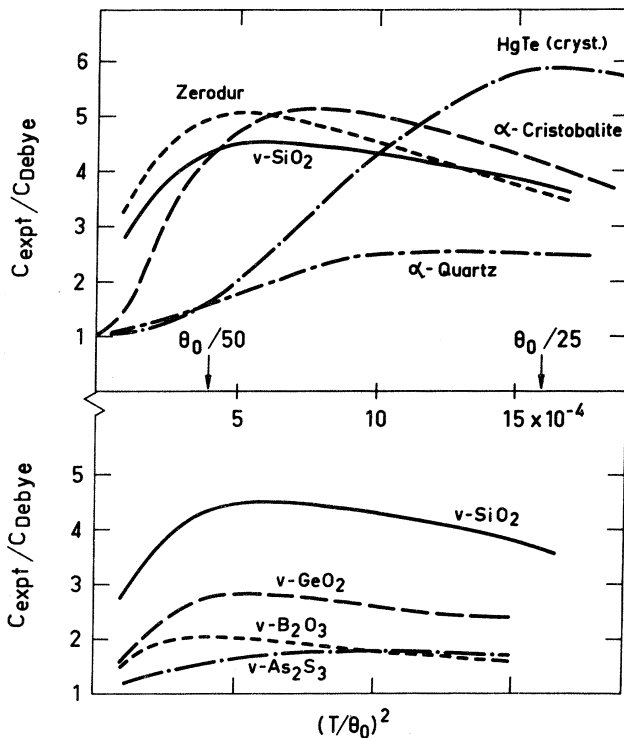


FIG. 3. Reduced plot of  $(C/T^3)_{\text{expt}}[(C/T^3)_{\text{Debye}}]^{-1}$  vs  $T/\Theta_0$  for selected solids [most references in Stephens (Ref. 10) or Pohl (Ref. 4)]: vitreous  $\text{B}_2\text{O}_3$  ( $\Theta_0 = 259 \text{ K}$ , present measurements); vitreous  $\text{As}_2\text{S}_3$  ( $\Theta_0 = 165 \text{ K}$ ); vitreous  $\text{GeO}_2$  ( $\Theta_0 = 495 \text{ K}$ );  $\alpha$ -quartz crystal ( $\Theta_0 = 560 \text{ K}$ );  $\alpha$ -cristobalite crystal ( $\Theta_0 = 475 \text{ K}$ ); Zerodur glass-ceramic ( $\Theta_0 = 530 \text{ K}$ ) (Ref. 19); HgTe crystal ( $\Theta_0 = 148 \text{ K}$ ) (Ref. 21).

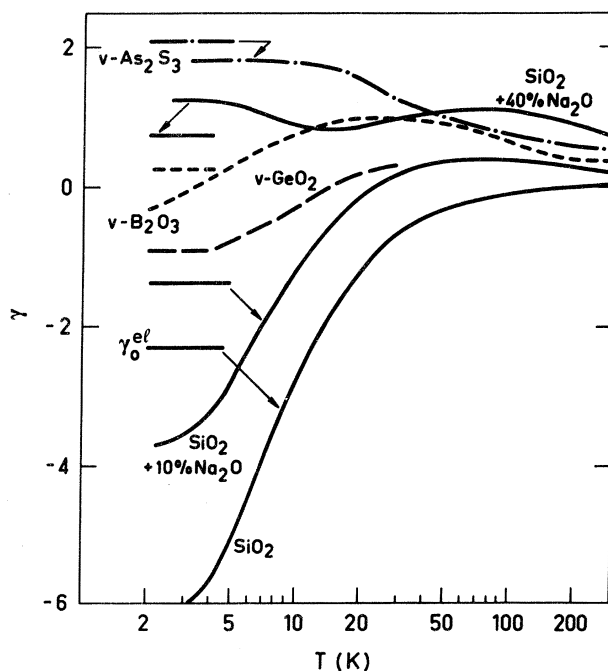


FIG. 4. Grüneisen parameter  $\gamma(T)$  for vitreous  $\text{B}_2\text{O}_3$  and  $\text{As}_2\text{S}_3$  (Ref. 13) compared with  $\text{SiO}_2$  and  $\text{SiO}_2\text{-Na}_2\text{O}$  glasses (Ref. 12) and  $\text{GeO}_2$  glass (Refs. 6 and 22). Horizontal lines indicate values of  $\gamma_0$  (elastic).

the oxygen atoms and torsional oscillations between the  $\text{SiO}_4$  tetrahedral contribute to negative expansion. The addition of a network filler like  $\text{Na}_2\text{O}$  (Ref. 12) or an increase in packing density (by heat treatment or neutron irradiation<sup>23</sup>) reduces the negative contribution, whereas merely modifying the network by replacing a few percent of Si by B atoms (as in Vycor) does not noticeably affect the expansion at low temperature.<sup>8</sup> An obvious difficulty is to explain why vitreous  $\text{GeO}_2$  does not show an anomalously large negative expansion. Clearly vitreous  $\text{As}_2\text{S}_3$  and  $\text{B}_2\text{O}_3$  show no evidence of negative expansion in the intermediate region above 3 K but do when tunneling states become important.

### SUMMARY

Present measurements of heat capacity of well-dried vitreous  $\text{B}_2\text{O}_3$  from 1.8 to 20 K agree with earlier values of

Jeapes and Leadbetter. The  $T^3$  component leads to a limiting value for the Debye temperature,  $\Theta_D^{\text{th}} = 259$  K which is somewhat smaller than that predicted from elastic constants,  $\Theta_D^{\text{el}} = 271$  K. There is no evidence of the tunneling or  $T$  term above 1.8 K. The linear expansion coefficient is negative below 3.3 K. It can be represented by a  $T + T^3$  expression only over a very restricted range from 1.8 to 3.5 K, where the magnitude of these terms leads to respective Grüneisen parameters of  $\sim -25$  ( $T$  term) and  $+0.3$  ( $T^3$  term).  $\gamma(T)$  is similar to that of  $\text{As}_2\text{S}_3$  above 40 K but not at lower temperatures.

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