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Tunneling models and the experimental thermal expansivities of fused silica and poly(methylmethacrylate) (PMMA) below 4 K

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Linear-thermal-expansivity data are given to 1.5 K for the two different amorphous solids, fused silica (amorphous SiO_2) and PMMA [poly(methylmethacrylate)]. Both solids exhibit a negative expansivity contribution at low temperatures which is linear in the absolute temperature and which corresponds to a common Grüneisen parameter, $\gamma_1 = -16$. A calculation is given for the corresponding expansivity which would be expected for a continuous distribution in energy of two-level states using both symmetric and asymmetric tunneling models. Inconsistencies between the postulates which must be made to explain the present results and those required to explain other low-temperature properties of amorphous solids lend support to the conclusion from other experiments that the tunneling model does not explain satisfactorily the low-temperature properties of amorphous solids.

I. INTRODUCTION

The low-temperature properties of amorphous solids show anomalous behavior[1] which can be interpreted in terms of a uniform distribution in energy of two-level systems.[2,3] This postulate can be used to "understand" a number of different experimental results, among them being a low-temperature heat-capacity contribution which is linear in the absolute temperature T and which is a few percent of that for one-electron metals. No direct evidence exists as to the nature of these two-level systems, although they have been postulated as originating from the tunneling of molecular complexes between two equivalent sites.[1-3] The existence of differences between the density of states as derived from heat capacity and a combination of transport and acoustic data[4] has led to the postulate of two types of tunneling states for fused silica (amorphous SiO_2).[5,6] A relatively small number of "standard" states (roughly 5% of the total) produce resonant scattering of phonons in thermal conductivity and pulsed phonon experiments, while the remaining "anomalous" states do not interact readily with phonons but are dominant for the heat-capacity contribution. A relaxation time which is associated with the anomalous states leads to the prediction that measured heat capacities should become smaller as the time scale of the measurement is decreased. This prediction was tested recently by Kummer, Dynes, and Narayanamurti,[7] who found no relaxation time effects in heat-capacity measurements on fused silica for which measuring times ranged from seconds to the submicrosecond level at temperatures from 50 mK to 3.8 K. They suggest concern about the validity of the tunneling model as it usually is proposed.

White[8] commented when presenting expansivity data for fused silica that low-temperature thermal-expansion measurements can provide a test for the tunneling hypothesis since this mechanism should result in an excessive thermal expansivity below 4 K. The basis for his remark involved large tunneling-related thermal-expansion anomalies which have been observed for dilute concentrations of OH^- and CN^- in NaCl and Li^+ in KCl.[9,10] The purpose of the present experiments was to obtain detailed thermal-expansion data below 4 K for two very different amorphous solids, fused silica and poly(methylmethacrylate) (PMMA or plexiglas), to investigate possible common behavior. An elementary calculation is used to demonstrate the manner by which tunneling can influence the low-temperature thermal expansion of a tunneling system and to provide a means for comparing quantitative predictions with experiment.

II. THERMODYNAMICS AND TUNNELING MODEL PREDICTIONS

The predictions of the tunneling model and the results of this experiment will be discussed in terms of the Grüneisen model, for which the volume expansion coefficient of a solid [the volume expansivity, $\beta = (\partial \ln V / \partial T)_p$] is related directly to the constant-volume heat capacity per unit volume (C_V/V) as[11]

$$\beta = \sum_i \beta_i = (B_T)^{-1} \sum_i \gamma_i \left(\frac{C_{Vi}}{V} \right), \qquad (1)$$

where B_T is the isothermal bulk modulus, the summation is over the various independent contributions to the free energy, and γ_i is the dimensionless Grüneisen parameter associated with each contribution. In this model, the heat capacity is given in reduced form as $C_{Vi}(\epsilon_i/k_BT)$, with

$$\gamma_i = -d\ln\epsilon_i/d\ln V. \tag{2}$$

The γ_i's typically are of the order of 3 ± 2 for normal excitation mechanisms in solids, but can have much larger magnitudes (of up to 300) for substitutional impurities in alkali halides.[9,10] Qualitatively, the large Grüneisen parameters for the impurity contribution in these systems are believed to be due to an extreme volume sensitivity of the tunnel splitting of the impurity ground state.

The low-temperature heat capacity per unit volume for a glass or amorphous solid is given approximately by[1]

$$C_V = a_1T + a_3T^3 + a_5T^5 \cdots = a_1T + (a_D + a_{\text{exc}})T^3 + \cdots , \tag{3}$$

where a_1 is associated with the two-level systems, a_D is the Debye contribution as calculated from sound velocity measurements, and a_{exc} represents an excess of the T^3 contribution over the normal lattice (Debye) term. Hence, from the form of Eq. (1), the low-temperature expansivity would be expected to be given by

$$\begin{aligned}\beta &= b_1T + b_3T^3 + b_5T^5 \cdots \\ &= (B_T)^{-1}[\gamma_1a_1T + (\gamma_Da_D + \gamma_{\text{exc}}a_{\text{exc}})T^3 + \cdots].\end{aligned} \tag{4}$$

The Grüneisen parameter for the excess contribution can be calculated from the difference between the experimental coefficient of the T^3 term, b_3, and γ_Da_D as obtained from sound velocity measurements as a function of pressure. The major concern of the present paper, however, will be with the coefficient b_1 and the Grüneisen parameter γ_1 for amorphous solids, although the γ_{exc} is also obtained from the data.

Phillips[12] has calculated this thermal expansion contribution for the tunneling model and an assembly of asymmetric double harmonic oscillators. The following discussion is consistent with and extends his results. First, the thermal expansion will be calculated for an assembly of identical symmetric double oscillator systems in terms of the parameters which describe these oscillators. This calculation should be related qualitatively to the results for impurities in alkali halides. Second, Phillips' result for the asymmetric double oscillator system will be reproduced in a simple extension of this calculation. Finally, a quantitative estimate will be made of the Grüneisen parameter γ_1 for each of these cases for fused silica and PMMA.

The tunnel splitting of the ground state for a symmetrical one-dimensional double oscillator system is given approximately by[13]

$$2\Delta_0 = 2\hbar\omega(\sigma/\pi)^{1/2}e^{-\sigma} \quad (\sigma > 2). \tag{5}$$

The characteristic dimensionless parameter σ is defined by

$$\sigma = 2V_0/\hbar\omega = m\omega l^2/\hbar , \tag{6}$$

where V_0 is the barrier height, ω is the characteristic frequency of a single harmonic oscillator which contains the mass m, and $2l$ is the spatial separation of the potential minima. A collection of identical two-level systems of this type will give a Schottky heat-capacity contribution with a maximum at $k_BT_{\max} = 0.834\Delta_0$.[14] The thermal expansion contribution, which also will be a maximum at this temperature, can be calculated using Eq. (1) and the expression for the Grüneisen parameter which follows from Eqs. (5) and (6),

$$\gamma(\Delta_0) = -d\ln\Delta_0/d\ln V = \gamma_\omega(\tfrac{3}{2} - \sigma) + \tfrac{2}{3}\sigma - \tfrac{1}{3} , \tag{7}$$

where $l^2 \propto V^{2/3}$. The oscillator frequency ω appears implicitly in Eq. (7) through the definition of σ [Eqs. (5) and (6)], while $\gamma_\omega = -d\ln\omega/d\ln V$ is an unknown parameter which would, however, be expected to be positive and similar in magnitude (3 ± 2) to other Grüneisen parameters.

Equation (7) implies, for normal positive values of γ_ω, that the Grüneisen parameter for a tunnel-split ground-state system should become increasingly more negative (a negative expansivity) as the potential barrier between the two oscillators becomes larger and the magnitude of σ increases. The doped alkali halides show the expected Schottky anomalies for C_V,[15] and the large magnitudes for the γ's associated with these anomalies. The Grüneisen parameter, however, is negative only for CN$^-$ in NaCl,[9] and is +40 for OH$^-$ in NaCl,[9,10] and +300 for Li$^+$ in KCL.[9] If our model is to relate to these more complex systems where the ground state may be tunnel split into three or four two-level states,[10] γ_ω must be negative for the Li$^+$ and OH$^-$ impurity systems and positive for CN$^-$.

The general case for a distribution in energy of two-level systems, as well as the extension of the above calculation to the asymmetric double harmonic oscillator model,[2,3,12] requires the use of general expressions for both the heat capacity and the Grüneisen parameter,

$$C_V = \int_0^{\epsilon_{\max}} C_V(\epsilon/k_BT)n(\epsilon)\,d\epsilon \tag{8}$$

and

$$\gamma = \frac{\int_0^{\epsilon_{\max}} C_V(\epsilon/k_BT)n(\epsilon)\gamma(\epsilon)\,d\epsilon}{\int_0^{\epsilon_{\max}} C_V(\epsilon/k_BT)n(\epsilon)\,d\epsilon} . \tag{9}$$

For low temperatures ($k_B T \ll \hbar\omega$), $\epsilon_{\max}$ can be taken as infinity, while, due to the form of the two-level expression for C_V, the lower limit of the integral effectively is zero as long as $n(\epsilon)$ and $\gamma(\epsilon)$ do not diverge too rapidly.

The Grüneisen parameter for an assembly of asymmetric double harmonic oscillators which are uniformly distributed in energy $[n(\epsilon)=n(\Delta_0)=n_0]$ can be calculated from Eqs. (7) and (9) using the mean-value theorem as

$$\gamma(\Delta_0=1.20\, k_B T)=\gamma_\omega(\tfrac{3}{2}-\sigma)+\tfrac{2}{3}\sigma-\tfrac{1}{3}\,, \tag{10}$$

since $C_V(2\Delta_0/k_B T)$ has a maximum at $2\Delta_0=2.40\, k_B T$.[14] The parameter σ [Eq. (5)] now is a function of $\Delta_0/\hbar\omega=1.20\, k_B T/\hbar\omega$, with the result that γ has a slight temperature dependence. The sensitivity of the experiments which are used to measure thermal expansivities at low temperature is sufficiently limited so that this slight temperature dependence possibly could not be observed.

The extension of the above calculation to an asymmetric double harmonic oscillator changes the results drastically. If 2Δ is the energy difference between the two minima, the characteristic energy ϵ is given by[2,3]

$$\epsilon^2=\Delta^2+\Delta_0^2\,, \tag{11}$$

and the Grüneisen parameter by

$$\gamma(\Delta,\Delta_0)=(\Delta^2/\epsilon^2)\gamma(\Delta)+(\Delta_0^2/\epsilon^2)\gamma(\Delta_0)\,. \tag{12}$$

Since both Δ and Δ_0 must take on a distribution of values for a given value of ϵ, $\gamma(\epsilon)$ must be calculated using assumed distribution functions for these two parameters. As Phillips stated,[12] the qualitative result is not very dependent on the forms of the distribution functions which are assumed, although these must be chosen so as to produce a heat capacity [Eq. (8)] which is approximately linear in T. Phillips[3,12] assumed that Δ is distributed uniformly in energy [$n(\Delta)$ a constant], with the distribution for Δ_0 [$n(\Delta_0)$] determined by a uniform distribution of barrier heights or, equivalently, a uniform distribution in energy of σ. He gives $n(\epsilon_0)\propto\Delta_0^{-1}$, and $n(\epsilon)\propto\ln(2\epsilon/\Delta_{\min})$, where $\Delta_{\min}$ has been introduced to prevent a singularity at $\epsilon=0$. This expression for $n(\epsilon)$, which applies for $\epsilon\gg\Delta_{\min}$, can be used in Eq. (8) together with the mean-value theorem to predict

$$C_V\propto k_B T\ln(2.40\, k_B T/\Delta_{\min}) \quad (k_B T\gg\Delta_{\min})\,. \tag{13}$$

This expression agrees well with the very-low-temperature (<0.1 K) heat-capacity data of Lasjaunias and collaborators for fused silica[16] and vitreous B_2O_3,[17] and enables estimates to be made of $\Delta_{\min}=3$ and 9 mK for two fused silica samples and $\Delta_{\min}=78$ mK for the B_2O_3 sample. The correspondence is not exact, however, with Eq. (13) seeming to apply at temperatures which are of the order of $\Delta_{\min}$.

Equation (12) now can be transformed using Phillips' distributions into the approximate relationship,

$$\gamma(\epsilon)=\gamma(\Delta)+[\gamma(\Delta_0=\epsilon)-\gamma(\Delta)]/\ln(2\epsilon/\Delta_{\min})\,. \tag{14}$$

The Grüneisen parameter for an assembly of such systems is calculated from Eq. (9) using the mean-value theorem and $\epsilon=1.20\; k_B T$ as

$$\gamma(T)=\gamma(\Delta)+\frac{[\gamma(\Delta_0=1.20\, k_B T)-\gamma(\Delta)]}{\ln(2.40\, k_B T/\Delta_{\min})}\,. \tag{15}$$

Equation (15) essentially is Phillips' result,[12] and forms the basis for his conclusion that explicit tunneling effects [those associated with $\gamma(\Delta_0)$] could not produce large magnitude expansivity anomalies at low temperature for the asymmetric tunneling model. The second term on the right is only approximate, but reflects the effects in Eq. (12) of the $(\Delta_0/\epsilon)^2$ weight of the large values of $\gamma(\Delta_0)$ which occur for the smallest values of Δ_0. We would argue that $\gamma(\Delta)$ should be "normal" (3 ± 2) since it is a consequence of normal lattice interactions.[18]

The magnitudes of these Grüneisen parameters [Eqs. (10) and (14)] can be estimated for a given amorphous solid by assuming $\gamma_\omega=3$ and a direct relationship[2] between the characteristic oscillator frequency and the glass transition temperature T_g, $\hbar\omega=k_B T_g$. Hence, with $T_g=1900$ K for fused silica and 430 K for PMMA, $\sigma=7.14$ for fused silica and 5.47 for PMMA at 2 K, and from Eq. (10), $\gamma(\Delta_0)$ is -12.5 and -8.6, respectively, for the two solids at this temperature. The corresponding value of γ_1 for the asymmetric model can be estimated for fused silica [Eq. (15), with $\Delta_{\min}\sim10^{-2}$ K from the heat-capacity results] to be of the order of unity. Hence, the tunneling contribution to γ_1 is diluted almost completely for this approximate asymmetric model calculation, with the low-temperature thermal expansion determined almost completely by $\gamma(\Delta)$. White's[8] results, which he interprets as giving $\gamma_1=-47\pm7$, suggest, however, that this prediction is not correct.

III. THE EXPERIMENT

The expansivities of PMMA and fused silica samples were measured with respect to copper using a capacitance dilatometer and three-terminal bridge system.[19,20] This dilatometer contained three identical copper reference samples which were located symmetrically about an unknown (center) sample on an oxygen-free high-conductivity copper base plate. Each sample was approximately 38 mm long and 15 mm in diameter, and was either electrically conducting or was coated with a thin metallic film. The dilatometer top plate contained four identical 10.5-mm diam guarded capacitor plates, one located above the center of each sample. This top plate was separated from the base plate by three posts which were made from single-crystal silicon and from PMMA for the fused silica and PMMA experiments, respectively. The lengths of the posts and the samples were chosen to produce capacitor gaps of approximately 0.1 mm at 4 K, with capacitances of approximately 4 pF (4×10^{-12} F). The thermometric and electrical details for this dilatometer[20] are very similar to those described elsewhere.[19]

The changes in the capacitances with temperature gave apparent expansivities for each sample with respect to the posts, while the differences in the gap changes gave apparent expansitivity differences between the various samples, with the assumption of a rigid top plate. The three copper samples gave the same gap changes to within 1% for temperatures above 4 K, which suggested that the top plate was moving parallel to the base plate. Differences appeared below 4 K, however, which were interpreted in terms of a tipping of the dilatometer as the vapor pressure of liquid helium in a small chamber above the dilatometer was reduced by pumping to achieve temperatures down to 1 K. This effect was of unknown origin, but it could be eliminated by applying corrections which were determined in an isothermal pressurization experiment at 6 K.

The dilatometer was calibrated by taking data for a polycrystalline silicon reference sample in the center position, with this sample made from the same material as that used by Lyon *et al.*[21] Results from that experiment were used to calculate the effective average linear expansivities for the present copper samples, "α_{Cu}", which are shown in Fig. 1, where they are compared with the relation given by Kroeger and Swenson.[19] The sensitivity of this dilatometer corresponds to approximately 5×10^{-11} K^{-1} in the linear expansivity [$\alpha=(\partial\ln L/\partial T)_p=\frac{1}{3}\beta$ for an isotropic solid], or roughly to the scatter of the results in Fig. 1. For reference, the expansitivities at 2 K for our two samples, fused silica and PMMA, are -2.7 and $+10$ times the value for "α_{Cu}" at 2 K in Fig. 1, with the ratios increasing in magnitude at higher temperatures. Hence, the differences from the earlier results which are shown in Fig. 1 are not serious, and may be considered to be due to a characteristic of the dilatometer. The copper samples were not disturbed between the calibration runs and the measurements with the amorphous samples.

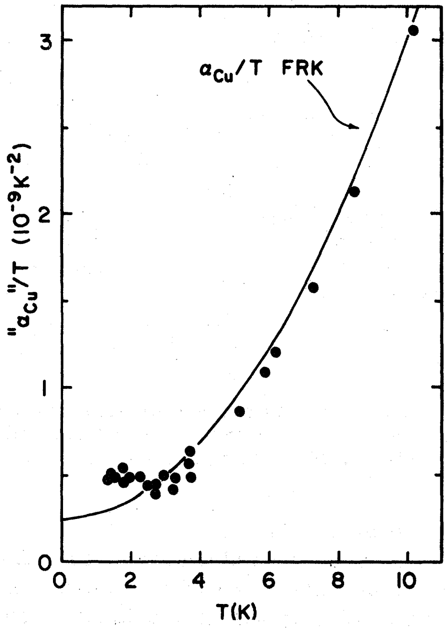

FIG. 1. Cell calibration data below 10 K, as discussed in the text. Also shown is the thermal expansion of copper given in Ref. 19.

The copper samples were made from material which should have been identical with that used by Kroeger (99.999+ % pure from the American Smelting and Refining Co.), and were treated in the same manner, including electron-beam melting and a high-temperature, high vacuum anneal. The fused silica sample (Spectrosil) was obtained from Thermal American Fused Quartz Co. of Montville, New Jersey. It corresponds closely to that used for other measurements of the heat capacity[22] and thermal expansion[8] of fused silica. The PMMA sample and posts were obtained from a commercial plexiglas rod. The samples were held to the base plate in a manner similar to that described by White and Collins.[23]

Figures 2 and 3 contain the experimental low-temperature results for the fused silica and PMMA samples, respectively. The data for PMMA were unambiguous, while those for fused silica initially showed considerable scatter (the solid points in Fig. 2) which appeared for temperatures below the ^{4}He λ point, 2.2 K. This scatter arose due to long-term (several hour) drifts which occurred after a change in temperature, and which did not appear in the PMMA or silicon experiments. These effects disappeared when the data were taken in the absence of exchange gas (the crosses in Fig. 2). White's data for fused silica,[8] which are plotted also in Fig. 2, show this same effect, although he does not report observing drifts. Heat-capacity data for fused silica[24] are affected by helium-gas absorption, with, however, no explicit differences

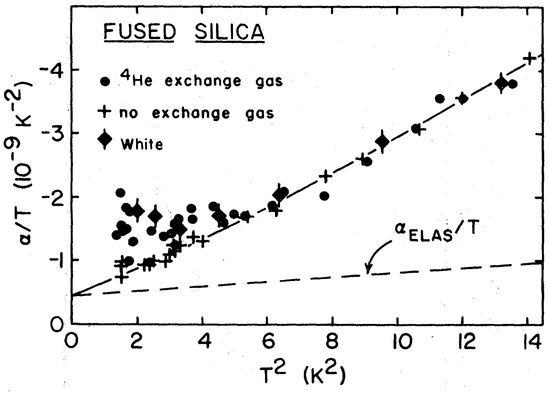

FIG. 2. Low-temperature linear-thermal-expansion data for fused silica as taken with and without exchange gas. White's data (Ref. 8) are also shown.

observed at the λ point.

The actual experimental data for these samples are given elsewhere.[20] Fused silica data were taken only to 10 K because of excellent agreement with White's[8] results up to this temperature. PMMA data were taken to room temperature because of previous data[25] which showed unusual behavior which we did not confirm. The solid lines in Figs. 2 and 3 are from smooth power-series representations of the data corresponding to Eq. (4) with $\alpha = \frac{1}{3}\beta$. The appropriate coefficients b_n which are given in Table I were determined by least-squares fits of Eq. (4) to the data. Smoothed expansivities are given for these samples in Tables II and III.

IV. DISCUSSION

Figures 2 and 3 show that the expansivities for both fused silica and PMMA have negative contributions at low temperature which are linear in the absolute temperature. The expansivities for fused silica are negative for all temperatures below approximately 100 K,[30] and are small in magnitude at high temperatures with the precise behavior dependent on heat treatment. The expansivities for PMMA are positive at all temperatures. Hence, a common feature for the expansitivities of these two amorphous solids, a negative contribution linear in T, only occurs at low temperatures, where the broad distribution of two-level states model is important.

The results can be discussed best in terms of the

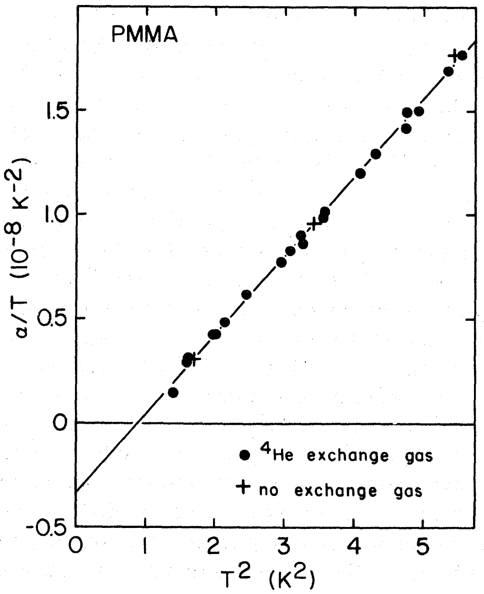

FIG. 3. Low-temperature ($T < 2.4$ K) linear expansion data for PMMA plotted as α/T vs T^2.

TABLE I. Summary of various parameters [Eqs. (1)–(4)], which are used to analyze this experiment, together with the experimental Grüneisen parameters γ_1, $\gamma_{3\,\mathrm{exc}}$, γ_5.

	Fused silica ($T < 3.5$ K)		PMMA ($T < 2.4$ K)	
Parameter (units)	Value	Reference	Value	Reference
B_T (10^{10} Nm^{-2})	3.50	26	0.82	27
a_1 (Jm^{-3} K^{-2})	3.04	22	5.28	28
a_3 (Jm^{-3} K^{-4})	2.53	22	32.2	28
a_{3D} (Jm^{-3} K^{-4})	1.69	29,20	21.5	27,20
$a_{3\,\mathrm{exc}}$ (Jm^{-3} K^{-4})	0.84	···	14.6	···
a_5 (Jm^{-3} K^{-6})	0.217	22	···	···
γ_{3D}	−2.29	26,20	4.25	27,20
b_1 (10^{-9} K^{-2})	−1.323	···	−10.56	···
b_3 (10^{-9} K^{-4})	−0.618	···	11.49	···
b_{3D} (10^{-9} K^{-4})	−0.102	20	11.16	20
$b_{3\,\mathrm{exc}}$ (10^{-9} K^{-4})	−0.516	···	0.33	···
b_5 (10^{-11} K^{-6})	−1.257	···	···	···
γ_1	−15.2 ± 0.8	···	−16.4 ± 2.1	···
$\gamma_{3\,\mathrm{exc}}$	−21.5 ± 1.2	···	0.2 ± 0.6	···
γ_5	−2.0 ± 0.4	···	(0)	···

TABLE II. Linear-thermal-expansion coefficient ($\alpha = \frac{1}{3}\beta$) for fused silica. A linear interpolation is accurate to 1% above 3.5 K, while the fit equation (see Table I) should be used for lower temperatures.

T (K)	α (K^{-1})
1	-0.65×10^{-9}
1.5	−1.40
2	−2.66
2.5	−4.73
3	−7.92
3.5	-1.26×10^{-8}
3.75	−1.54
4	−1.85
4.5	−2.64
5	−3.62
5.5	−4.83
6	−6.25
7	−9.69
8	-1.37×10^{-7}
9	−1.79
10	−2.24

Grüneisen model which is defined by Eqs. (1)–(4). The data which are required for this discussion as well as the sources of these data are given in Table I together with the resulting Grüneisen parameters. Very briefly, the results can be summarized as follows:

TABLE III. Linear-thermal-expansion coefficients for PMMA ($\alpha = \frac{1}{3}\beta$). A linear interpolation is accurate to 1% above 2.4 K, while the fit equation (see Table I) should be used below 2.4 K.

T (K)	α (K^{-1})	T (K)	α (K^{-1})
1.5	0.77×10^{-8}	25	1.13×10^{-5}
2	2.36	30	1.37
2.5	5.29	35	1.59
2.75	7.47	40	1.80
3	1.02×10^{-7}	45	1.98
3.25	1.35	50	2.14
3.5	1.73	60	2.41
4	2.69	70	2.64
4.5	3.87	80	2.83
5	5.28	90	3.01
5.5	6.89	100	3.17
6	8.68	120	3.48
6.5	1.065×10^{-6}	140	3.75
7	1.29	160	4.01
7.5	1.40	180	4.35
8	1.74	200	4.86
9	2.25	220	5.56
10	2.79	240	6.34
12	3.93	260	7.06
14	5.07	280	7.68
16	6.29	290	7.90
18	7.46	295	7.95
20	8.61	300	(8.00)

(i) The Grüneisen parameters (γ_1) which are associated with the "tunneling" region have the same negative sign and large magnitude for these two quite different solids. This result is remarkable in view of the very great differences in the lattice heat capacities and bulk moduli, and suggests an additional correlation which a theory of the amorphous state must satisfy. The much greater magnitude for γ_1 which was reported by White[8] for fused silica most likely is due to exchange gas effects which were not detected by him.

(ii) The Debye (acoustic) contributions to the heat capacity and the expansivity were calculated from data for the pressure dependence of the sound velocities,[20] with the fused silica data being somewhat more reliable than those for PMMA. The resulting Debye model Grüneisen parameters are given in Table I together with those which are associated with the excess T^3 contribution [γ_{exc}, Eqs. (3) and (4)]. The analysis of the PMMA results may not be straightforward since an Einstein mode, which becomes important for the heat capacity above 2.4 K,[31] also is apparent in the expansivity data and could effect the results below 2.4 K.

The experimental result that $\gamma_1 = -16$ for these two solids is very similar to the predictions which were made in our discussion of the symmetric tunneling model in Sec. II. Equation (10) can be used with the parameters introduced in that discussion to calculate the magnitude of γ_ω which would be required to give $\gamma_1 = -16$ for each solid. The results, $\gamma_\omega = 3.8$ for fused silica and $\gamma_\omega = 4.8$ for PMMA, are "reasonable," and lend credence to a postulate that the low-temperature expansivity for amorphous solids can be understood in terms of a symmetric tunneling model.

This conclusion clearly is at variance with the ultrasonic results, however, which demonstrate that only a few percent of the tunneling states can be described as symmetric,[4] and thus points out an additional problem with the tunneling model. This problem could be resolved if $\gamma(\Delta)$ were to be large and negative [Eq. (11)], but no mechanism other than tunneling has been shown to be capable of producing Grüneisen parameters of the required magnitude, so this postulate is not viable.

As was suggested by Phillips[12] and White,[8] low-temperature expansivity data can provide a rigorous test of theoretical models, since through the Grüneisen parameter they give a measure of the volume dependence of the energy levels which are excited at a given temperature. The present experiments at the very least suggest that any model of the low-temperature properties of amorphous solids must result in a negative Grüneisen parameter of relatively large magnitude, with $\gamma_1 \sim -16$.

In addition, if our calculations are even approximately correct, our results support the conclusions of Kummer *et al.*[7] that current theories which are based on asymmetric tunneling states cannot provide a consistent interpretation of the low-temperature properties of amorphous solids.

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