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Low-temperature thermal expansion of disordered solids

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The thermal-expansion coefficients α of vitreous silica, neutron-irradiated vitreous silica, vitreous silica containing OH^- or K_2O, the amorphous polymers SC5 (Scotchcast 5 epoxy, 3M Company) and PMMA, (polymethylmethacrylate) the chalcogenide glass As_2S_3, glassy PdSiCu, and crystalline samples of Na β-alumina and ZrO_2:Y_2O_3 have been measured to temperatures $T \lesssim 1$ K. The low-energy excitations generally found in glassy materials influence or dominate α at $T < 1$ K. However, unlike the specific heat and other properties, α is not a universal property of glasses. The α associated with the excitations may be large or small, positive or negative. The results may be explained provided the excitations exhibit a broad spectrum of deformation potentials in addition to a broad spectrum of energies.

I. INTRODUCTION

The low-temperature properties of amorphous materials have been subjected to extensive experimental and theoretical investigation for over a decade.[1] A large body of evidence has been gathered from which two fundamental observations can be made: (1) Below ≈ 1 K, the thermal or acoustic properties of most amorphous dielectrics are qualitatively similar in magnitude and temperature dependence, and (2) this signature of the glassy state is markedly different from that of pure dielectrics in the crystalline state. One theoretical model[2,3] of glassy materials has emerged which appears to fit experimental observations. In its present form, this phenomenological model proposes the existence of a broad energy band of localized excitations which may couple strongly to phonons. The excitations are characterized as having a ground state and one excited state which is well separated from states of higher energy, hence the name two-level systems (TLS). Tunneling of some entity or configuration between two potential-energy minima, separated by a large barrier as in Fig. 1, is cited as a possible origin of the TLS. However, the microscopic origin of TLS, whether from tunneling or by a different mechanism, has not been established for any amorphous material.

A proposed test of the tunneling nature of the TLS is a measurement of the TLS contribution to thermal expansion.[4] This suggestion is based in part on the observation that, in crystals containing impurities, the expansion coefficient can be large if the impurity reorients by tunneling.[5] In a discussion of thermal expansion,[6] it is convenient to use the Grüneisen parameter Γ defined as

$$\Gamma = 3B\alpha/C\ , \tag{1}$$

where B is the elastic bulk modulus, α is the coefficient of linear thermal expansion, and C is the specific heat per unit volume. For phonons $|\Gamma| \approx 2$ while, for crystalline impurities with associated tunneling states,[5] Γ may have a magnitude as large as 300. Hence, if tunneling does give rise to TLS in amorphous solids, the Γ of glasses might be anomalously large. Experimental measurements[4,7–9] of the thermal-expansion coefficients of glassy materials (at temperatures above $T \approx 1.5$ K) have indicated a large, negative Γ for TLS with $|\Gamma| \gtrsim 20$. This result has been taken as evidence that tunneling is indeed responsible for TLS. It has also been suggested[7,8,10] that a large negative Γ may be characteristic of glassy solids, and that Γ (or α) is an additional universal property of the amorphous state.

A few calculations of Γ have been made based on models of TLS. A negative Γ has been obtained[10,11] from a roton model, but this model has not achieved wide acceptance. The tunneling model of TLS, explicitly assuming a double-well potential as shown in Fig. 1 and discussed in Sec. II, does not presently provide a consistent explanation for a Γ of large magnitude.[12] Hence, theory has been of limited assistance in understanding the experimental data.

The suggestion of a universal Γ for glassy solids, discussed above, is based on measurements made only at $T \gtrsim 1.5$ K. It is primarily at lower temperatures that TLS make the strongest contribution to thermal properties. We have measured thermal-expansion coefficients to temperatures below 1 K to observe directly the influence of TLS on α. The materials investigated include oxide glasses, a chalcogenide glass, a metallic glass, amorphous polymers, and disordered single crystals which otherwise exhibit glassy behavior at temperatures below ≈ 1 K. We find,[13] contrary to expectation, that the Γ associated with TLS may be large or small, positive or negative.

II. TUNNELING MODEL OF A TLS

We adopt the notation of Ref. 1 in discussing the tunneling model. As usual, the double harmonic oscillator of Fig. 1 will be used so as to simplify the computations. In Fig. 1, V is the potential energy experienced by some entity having configurational coordinate x. When the asym-

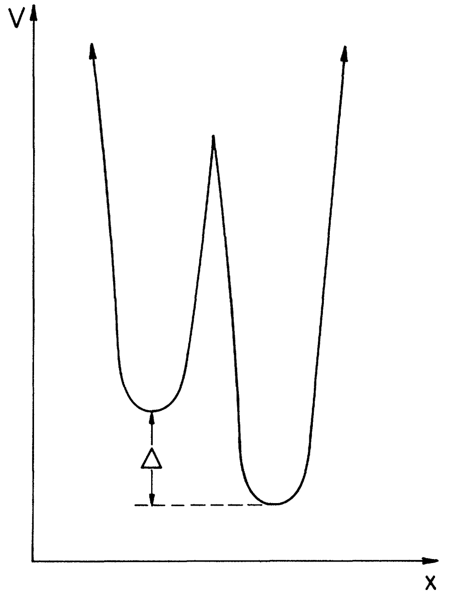

FIG. 1. Potential-energy double well used in the tunneling model of TLS.

metry energy Δ is zero, the energy splitting (caused by tunneling) of the degenerate ground state will be defined as Δ_0. The total splitting is then

$$E=(\Delta^2+\Delta_0^2)^{1/2}\ . \tag{2}$$

The potential wells must be sufficiently decoupled so that the first excited state of a single well lies well above the split ground state. Then the tunnel-split ground state can represent a TLS as required for the model. The model further assumes a broad distribution over Δ and Δ_0 for the ensemble of TLS.

A perturbation of the potential of Fig. 1 by a mechanical strain of amplitude e can be expressed by the deformation potentials[14]

$$D=\frac{\Delta}{E}\frac{\partial\Delta}{\partial e}+\frac{\Delta_0}{E}\frac{\partial\Delta_0}{\partial e}\ , \tag{3}$$

$$2M=-\frac{\Delta}{E}\frac{\partial\Delta_0}{\partial e}+\frac{\Delta_0}{E}\frac{\partial\Delta}{\partial e}\ . \tag{4}$$

The parameter D is a measure of the variation of energy splitting with strain, while M gives the strength of coupling between ground and excited state due to strain. In analogy with the computation of the linear expansion coefficient α for crystals, a Grüneisen equation of state can be formulated for a glass as

$$3\alpha B=\Gamma C(T)\ ,$$

in which B is the elastic bulk modulus, and

$$\Gamma=\sum_i \Gamma_i C_i \Big/ \sum_i C_i\ . \tag{5}$$

Here C_i is the contribution to the specific heat by the TLS at site i and $\Gamma_i=-(\partial \ln E_i/\partial \ln V)$ is the Grüneisen parameter for this TLS. Thus

$$\Gamma_i=-\frac{1}{E}\left[\frac{\Delta}{E}\frac{\partial\Delta}{\partial e}+\frac{\Delta_0}{E}\frac{\partial\Delta_0}{\partial e}\right]\Bigg|_i=\frac{D_i}{E_i}\ . \tag{6}$$

The strain derivatives appearing in Eq. (6) are unknown parameters in this model.

There is disagreement concerning the relative importance of the two derivatives in Eq. (6). It has been argued that $\partial\Delta_0/\partial e$ is small,[15] with estimates of $|\Gamma_i|$ arising from this term ranging[16,7] from ~ 1 to ~ 10. In the latter case, $|\Gamma_i| \approx 10$ was obtained for a symmetric tunneling model, i.e., $\Delta=0$ for most TLS. This requirement would appear to be inconsistent with resonance experiments.[17] It has also been suggested that $\partial\Delta_0/\partial e$ may be large.[18] This speculation is not based on an explicit model such as Fig. 1, but rather on experimental observations of large $\partial\Delta_0/\partial e$ for tunneling states in doped crystals. The derivative $\partial\Delta_0/\partial e$ will be large if the tunneling barrier in Fig. 1 is assumed to be low and wide,[8] but in this case the ground and excited states are not well separated from higher-energy states and a TLS model no longer exists. There is also no agreement concerning the contribution to Γ from the derivative $\partial\Delta/\partial e$. It has been argued[7] that this contribution arises from normal lattice interactions and thus should give $|\Gamma_i| \approx 3$. Alternatively, an argument has been made that $|\Gamma_i|$ could be large because of a change in the "local environment."[15]

A computation of the derivatives, and thence of Γ_i, from a microscopic model can be avoided by adopting the relation $\Gamma_i=D_i/E_i$ and treating D_i as a phenomenologically adjustable parameter. As a first approximation, let $D_i=D$, a constant. This procedure has been used in the past, even though it was recognized[15] that D (and M) is probably dependent on E. The magnitude of D may be obtained from ultrasonic measurements,[1] $|D| \approx 1$ eV$\approx 10^4$ K. By using this value in Eq. (5) we obtain[16,19]

$$|\Gamma|=\frac{D\sum C_i/E_i}{\sum C_i}\approx\frac{D}{E}\Bigg|_{E\approx T}\approx\frac{D}{T}\approx\frac{10^4}{T}\ . \tag{7}$$

Since the result of this computation is widely different than that observed for any glassy material, D_i cannot be a constant if the otherwise useful tunneling model is to be retained. The D_i must change in sign, and probably in magnitude, at different TLS sites. We will return to this question following a discussion of our experimental results.

III. MEASUREMENT TECHNIQUE

The dilatometer has been discussed previously[20] and will only be reviewed briefly here. If L (2–3 cm) is the length of the sample, then $\alpha=(1/L)dL/dT$. We measure dL/dT directly by imposing on the sample a square-wave modulation dT of the temperature. The resulting periodic variation of L causes an attached superconducting coil to move in and out of a fixed magnetic field. The currents induced in the coil are detected with a superconducting quantum interference device (SQUID) and the SQUID output is signal averaged to improve the signal-to-noise ratio. Resolution of this dilatometer is 2×10^{-4} Å.

A small fixed coil placed near the superconducting coil attached to the sample allows the net gain of the SQUID and electronic components to be checked each run. This gain never changes. A small piezoelectric transducer is attached to the end of the sample and thus can also move the superconducting coil. With this transducer it is possible to check whether SQUID output versus dL is independent of temperature. The transducer also provides a direct, *in situ* calibration of the dilatometer. The transducer produced the expected displacement for a given applied voltage, and this displacement agreed with that produced by pure copper when used as a thermal-expansion standard. Unfortunately, after a period of some months, the transducer ceased to function properly, and the motion provided by the transducer often changes upon thermal cycling; therefore, the dilatometer calibration is now checked frequently using a sample of high-purity copper.[20] In brief, we can accurately determine the temperature dependence of the thermal-expansion coefficient, but the magnitude of α is uncertain. Statistically, this uncertainty in magnitude is found to be about $\pm 20\%$.

We have observed one problem which is common to both the capacitive and SQUID dilatometers, namely the deleterious effect of a small quantity of residual ^{4}He gas within the cryostat which forms a film on all surfaces. In the capacitive dilatometer[7] the film itself probably responds to the applied ac electric field in the capacitor, thus creating a spurious indication of sample expansion. In the SQUID dilatometer, such a film thermally bridges components which should be thermally isolated. In our cryostat, such a problem developed when, after roughly two years of operation, a leak appeared in the heat exchanger of a commercial dilution refrigerator. The leak rate was $\approx 10^{-7}$ cm^3/sec (STP) and could be observed only on cooling below 80 K. After some days of operation, sufficient ^{4}He would accumulate to provide thermal contact between sample and other dilatometer parts. These components would then track the temperature of the sample and cause a spurious signal[20] in the SQUID output, primarily for temperatures $\gtrsim 1$ K. The temperature fluctuations were detected with carbon-resistance thermometers. The film could be removed for a few days by "baking" the refrigerator and dilatometer at $T \gtrsim 10$ K, but the proper solution was repair of the leak. No data were obtained while the leak was present.

IV. RESULTS

In most of the following examples the measured expansion coefficient α has been divided by T^3 to emphasize departures from the T^3 temperature dependence expected from thermal phonons at low temperatures. In addition we also present an empirical Grüneisen parameter Γ obtained from Eq. (1) using smoothed values of α and of the specific heat C. Plots of Γ are limited to a temperature range for which both α and C are available. The bulk modulus B of Eq. (1) was obtained from measured sound velocities and mass densities.

A. Silicate glasses

The thermal-expansion data for silicate glasses are displayed in Fig. 2. In all cases the thermal expansion is negative. Included in Fig. 2 are Spectrosil WF,[21] a high-purity vitreous silica (≈ 20 ppm OH$^-$), Spectrosil B[21] containing ≈ 1200 ppm OH$^-$, Spectrosil B irradiated[22] with 5×10^{19} neutrons/cm^2, and vitreous silica[23] containing 10 mol % K_2O. The high-temperature data agree qualitatively with previous measurements[4,7] on vitreous silica as shown by the solid lines. The factor of ≈ 2 reduction in $|\alpha|$ resulting from addition of 10 mol % K_2O is close to that observed for SiO_2:Na_2O glasses.[24]

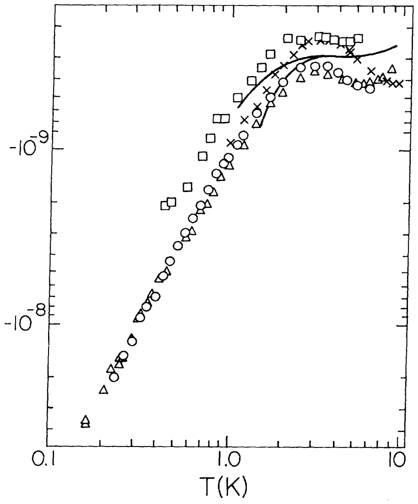

FIG. 2. Negative thermal-expansion coefficient α of silicate glasses divided by T^3, the cube of the temperature, to emphasize nonphonon contributions. ○—Spectrosil WF (high-purity SiO_2); △—Spectrosil B containing ≈ 1200 ppm OH$^-$; ×—Spectrosil B, neutron irradiated; □—SiO_2 containing 10 mol % K_2O; upper solid line—data of Ref. 7 on SiO_2; lower solid line—data of Ref. 4 on SiO_2.

The Grüneisen parameter Γ is shown in Fig. 3 for the silicate glasses.[25–27] At high temperature there is qualitative agreement with direct measurements[28,29] on vitreous silica using $\Gamma = -(V/T)dT/dV$. These measurements are shown as the dotted lines.

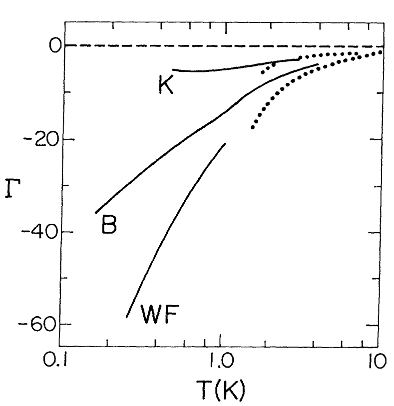

FIG. 3. Grüneisen parameter Γ for silicate glasses. WF—spectrosil WF; B—Spectrosil B (and, for 1–2 K, neutron-irradiated Spectrosil B); K—vitreous silica plus 10 mol % K_2O; dotted lines—direct measurements of Γ for vitreous silica (upper line Ref. 29, lower line Ref. 28).

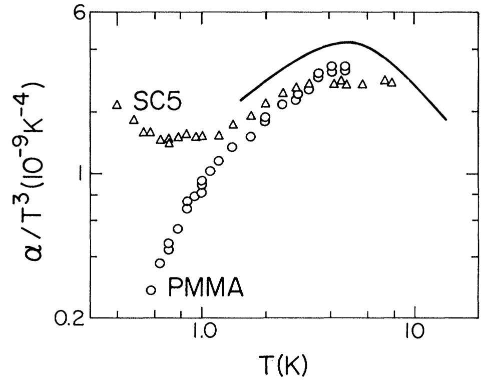

FIG. 4. Thermal-expansion data, divided by T^3, for two amorphous polymers. △—SC5 epoxy; ○—PMMA; solid line—PMMA from Ref. 7.

B. Amorphous polymers

Figure 4 shows α/T^3 for polymethylmethacrylate[30] (PMMA) and for an epoxy[31] designated as SC5. At high temperatures our data for PMMA lie 25% below earlier results[7] obtained on a different sample. The Grüneisen parameters are displayed in Fig. 5.

C. Chalcogenide glass

The thermal-expansion coefficient of the amorphous semiconductor As_2S_3 is shown in Fig. 6. At high temperatures the data are in agreement with earlier measurements (the solid line) made on a companion sample.[32] The Grüneisen parameter is shown in Fig. 7 together with earlier determinations.[33] The dashed extension for our data indicates the approximate Γ obtained if we use the unpublished specific-heat data utilized in Ref. 8.

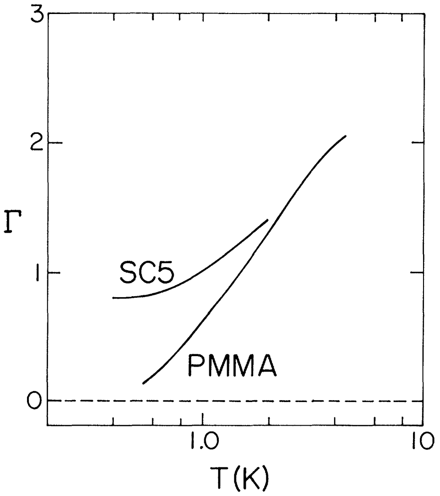

FIG. 5. Grüneisen parameters Γ for two amorphous polymers, PMMA and the epoxy SC5.

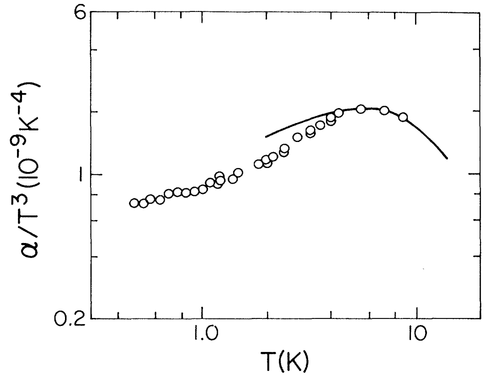

FIG. 6. Thermal-expansion coefficient, divided by T^3, of glassy As_2S_3. Solid line is taken from Ref. 8.

D. Glassy metal

The thermal-expansion coefficients for glassy $Pd_{0.775}Si_{0.165}Cu_{0.06}$ rods of 0.2 cm diameter are shown in Fig. 8. The circles represent data taken on a sample that was revealed to be amorphous by electron diffraction, and the presence of TLS was demonstrated through the characteristic temperature dependence of the ultrasonic velocities.[34] To learn if the presence of hydrogen impurity would influence α, this sample was remounted in the dilatometer, exposed to gaseous H_2 at 1 atm pressure and room temperature for a period of one week,[35] quickly cooled while maintaining the H_2 pressure, and then remeasured. These data are represented by triangles in Fig. 8. The presence of hydrogen in the sample did not change α. Finally, the α of a second rod, showing a small fraction of crystallinity in x-ray diffraction, is represented by the crosses in Fig. 8. Within the resolution of our measurement, the slight crystallinity of this less-rapidly-quenched sample did not change the expansion coefficient.

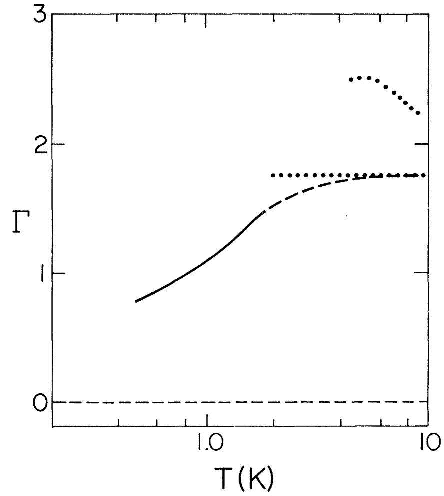

FIG. 7. Grüneisen parameter for glassy As_2S_3. Upper dotted line—data from Ref. 23; lower dotted line—data from Ref. 8. Dashed extension to our data is explained in the text.

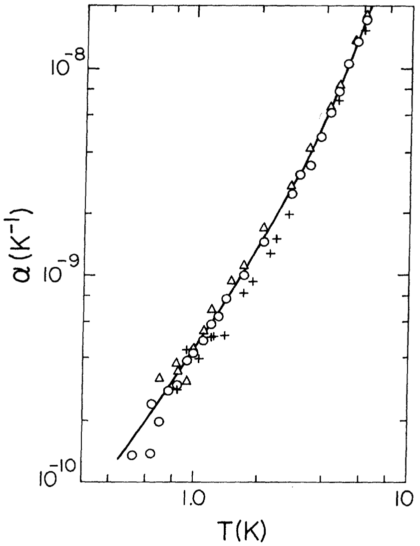

FIG. 8. Thermal-expansion coefficient of glassy PdSiCu rods. ○—amorphous sample; △—same sample exposed to gaseous H_2 prior to cooling; +—sample showing some crystallinity.

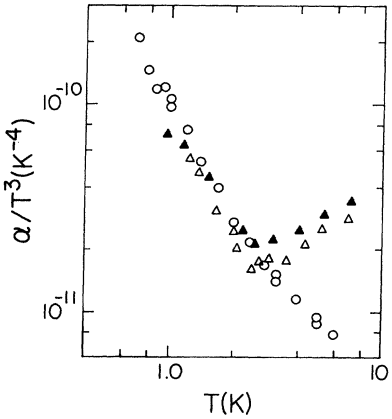

FIG. 10. Thermal-expansion coefficient, divided by T^3, for two crystalline fast-ion conductors. ○—ZrO_2:Y_2O_3; △—Na β-alumina (two independent runs).

The expansion coefficient of the two runs on the first rod was approximated by the solid line of Fig. 8, and this smoothed result was replotted in the form α/T vs T^2 in Fig. 9 for comparison with a previous measurement[36] represented by the dashed line. The highly anomalous behavior depicted by the dashed line has not been reproduced in our data.

E. Disordered crystals

Figure 10 shows the thermal-expansion coefficient, divided by T^3, for two disordered crystals, namely the fast-ion conductors Na β-alumina and cubic zirconia. The latter is ZrO_2 stabilized in the cubic phase through addition of 16 mol % Y_2O_3.

The Na β-alumina is highly anisotropic. The measurement of α was made along a direction perpendicular to the crystalline *c* axis. Samples oriented parallel to *c* were not available. The smoothed Grüneisen parameters[37,38] are presented in Fig. 11. There are no published data with which to compare our results.

V. DISCUSSION

We first make some comments specific to individual materials, then follow with a more general discussion of the results.

A. Silicate glasses

The thermal-expansion coefficient of vitreous silica, Fig. 2, is negative[39] at all temperatures below 150 K. However, only below ≈4 K does the Grüneisen parameter, Fig. 3, become large[40] ($|\Gamma| > 4$) relative to that expected from thermal phonons. It has been assumed that the large negative Γ at lower temperatures is associated with the localized TLS. Support for this assumption

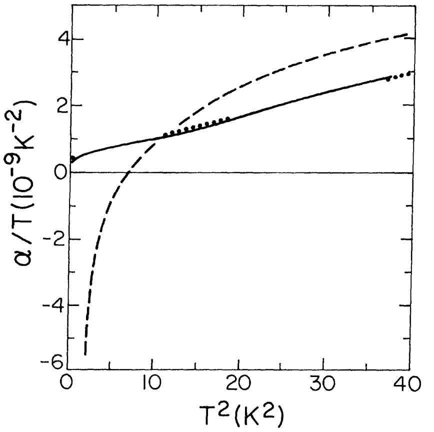

FIG. 9. Expansion coefficient for glassy PdSiCu plotted as α/T vs T^2. Dashed line is from Ref. 36. Solid line represents the fit to data as shown in Fig. 7, while the dotted line is the linear fit discussed in the text.

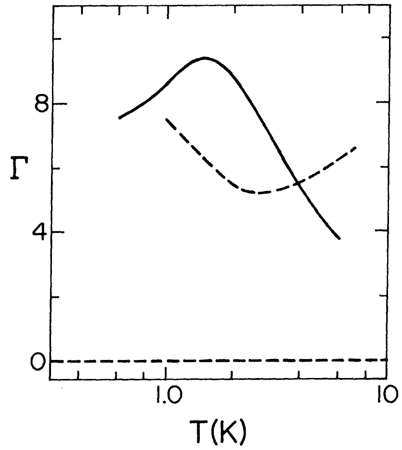

FIG. 11. Grüneisen parameters for two disordered crystals. Dashed line—Na β-alumina; solid line—ZrO_2:Y_2O_3.

comes from the neutron-irradiation data presented here. Neutron irradiation for this sample was previously observed[22] to change the specific heat, the thermal conductivity, and the temperature dependence of ultrasonic velocity by 30–40%, all consistent with a 30–40% decrease in the density of TLS. Thus the apparent $\approx 35\%$ reduction in $|\alpha|$ with irradiation,[41] without an accompanying change in Γ, suggests that the thermal expansion of SiO_2 glass is indeed dominated by TLS below ≈ 2 K.

Addition of ≈ 1200 ppm OH^- to vitreous silica was observed[42] to increase the low-temperature specific heat by $\approx 30\%$. Likewise, the specific heat of our Spectrosil B was larger than that of pure Spectrosil WF by a factor of about 1.4. Caution must be observed when comparing different samples of vitreous silica since the low-temperature properties also depend on thermal history.[39,43] Nevertheless, it will be assumed in the following that the presence of OH^- does increase the specific heat of vitreous silica.

We can obtain information concerning the deformation potentials associated with the TLS created by the addition of OH^-. The specific heat is proportional to the density $n(E)$ (per unit energy interval) of TLS. A specific heat roughly linear in temperature, as for the materials discussed in the present paper, is indicative of an $n(E)$ nearly independent of energy. In Spectrosil WF there exists a density $n_{\rm int}$ of TLS intrinsic to vitreous silica. If we assume that $n_{\rm int}$ is the same in Spectrosil B, then the specific-heat results indicate that the presence of OH^- adds a contribution $n_{\rm OH} \approx 0.4 n_{\rm int}$. The thermal-expansion coefficient is proportional to nD, provided the deformation potential D is treated as a constant. (We begin the discussion with this simplifying assumption that D is a constant, and will indicate later the problem which develops when using this assumption.) Since $\Gamma \propto \alpha/C$, the Grüneisen parameter for Spectrosil B is

$$\Gamma_{\rm B} \propto (n_{\rm OH} D_{\rm OH} + n_{\rm int} D_{\rm int})/(n_{\rm OH} + n_{\rm int}) \ . \tag{8}$$

Figure 3 indicates that $\Gamma_{\rm B} \approx 0.6 \Gamma_{\rm WF}$, and hence $D_{\rm OH} \approx -0.4 D_{\rm int}$. No other comparisons of $D_{\rm OH}$ and $D_{\rm int}$ are available. However, it has been observed that, for vitreous silica, D and M are of the same magnitude[1,15] for the intrinsic TLS. Several ratios of $M_{\rm OH}$ to $M_{\rm int}$ are available, and these may be used for comparison with $D_{\rm OH}$ vs $D_{\rm int}$. Estimates of M may be obtained from measurements of the thermal conductivity $\kappa \propto (nM^2 v^2)^{-1}$, where v is a phonon velocity. Since v changes very little with addition of OH^- to vitreous silica, we can use the changes in n (from C)[26] and in M^2 (from κ)[42] with the addition of OH^- to obtain $(M_{\rm OH}^2)^{1/2} \approx \pm 0.6 (M_{\rm int}^2)^{1/2}$. The OH^- also influences ultrasonic dispersion,[42] from which the authors obtain $(M_{\rm OH}^2)^{1/2} \approx \pm 0.3 (M_{\rm int}^2)^{1/2}$. Electric-echo observations[44] give $(M_{\rm OH}^2)^{1/2} \approx 0.6 (M_{\rm int}^2)^{1/2}$. Thus all of the measurements relating to M or D suggest that addition of ≈ 1000 ppm OH^- to vitreous silica simply adds a new population of TLS. The coupling of the OH^--related TLS to strain or phonons is roughly one-half that of the intrinsic TLS in vitreous silica. In addition, the sign of D for OH^- states is found to be positive, or opposite that of the intrinsic TLS.

Addition of 10 mol% K_2O to vitreous silica increases the low-temperature specific heat by a factor of 4.5, decreases κv^2 by a factor of 1.7, and decreases α by a factor of ≈ 2. If it is assumed that, as for OH^-, the K_2O content introduces a new population n_{K_2O} of TLS, then the analysis used above gives $D_{K_2O} \approx +0.1 D_{\rm int}$ from thermal-expansion data, but $(M_{K_2O}^2)^{1/2} \approx \pm 0.45 (M_{\rm int}^2)^{1/2}$ from the thermal conductivity. Unlike the SiO_2:OH comparison, these data were obtained for the same sample. The failure to obtain better agreement suggests that the relationship between D and M is different for the K_2O population than for the instrinsic TLS, and/or that the presence of 10 mol% K_2O has appreciably modified the SiO_2 matrix so that the TLS of the "intrinsic" population have been modified. Indeed, it may not be reasonable to divide n into $n_{\rm int}$ and n_{K_2O} for this large content of K_2O. If the SiO_2:K_2O does contain a single population $n_{\rm new}$, then we obtain $D_{\rm new} \approx +0.4 D_{\rm int}$ from α and $(M_{\rm new}^2)^{1/2} \approx \pm 0.4 (M_{\rm int}^2)^{1/2}$ from κv^2. The agreement suggests that the TLS in SiO_2:K_2O should be treated as a single homogeneous population.

B. Amorphous polymers and As_2S_3

The two polymers and the As_2S_3 have qualitatively the same expansion coefficient at $T \gtrsim 2$ K, with a Grüneisen parameter approaching the value $\Gamma \approx 2$. This behavior perhaps reflects a dominant contribution to α by thermal phonons for $T \gtrsim 2$ K. Below 1 K the three materials exhibit very different behavior which is presumably related to the TLS. For SC5, α/T^3 increases with decreasing T, for PMMA it decreases, while, for As_2S_3, α/T^3 is nearly temperature independent.

The M^2 of A_2S_3 has been measured by an electric-echo technique.[45] The result may be compared to that for vitreous silica obtained with the same technique, giving $(M_{As_2S_3}^2)^{1/2} \approx \pm 0.6 (M_{SiO_2}^2)^{1/2}$. Our expansion data suggest that $D_{As_2S_3} \approx -0.01 D_{SiO_2}$. Either M and D are very different for glassy As_2S_3, unlike vitreous silica, or $(M^2)^{1/2}$ is very different from M indicating that different M_i apply at individual TLS sites. The later possibility is discussed below.

C. Glassy metals

The large negative excursion of the dashed curve at low temperatures in Fig. 9 was interpreted in Ref. 36 as arising from TLS having a huge negative Grüneisen parameter. Our data, on the other hand, give no indication of an unusually large Γ. Near 1 K, α is an order of magnitude smaller for glassy PdSiCu than for the other amorphous solids reported here. Indeed the temperature dependence of the present data is close to $\alpha = (4.1 \times 10^{-10}) T + (6.5 \times 10^{-11}) T^3$ (K^{-1}) as represented by the dotted line in Fig. 9. This α is similar to that found for normal crystalline metals such as Pd. The specific heat of glassy PdSiCu may also be expressed as $C = \beta T + \gamma T^3$ as shown in Ref. 46. The linear terms in α and C arise primarily from the conduction electrons, while the cubic terms are ascribed primarily to phonons. Individual Grüneisen parameters may be associated with the linear and cubic terms via Eq. (1). We obtain $\Gamma_{\text{electron}} = +1.6$ and $\Gamma_{\text{phonon}} = +2.5$. These may be compared, for example, with the values $\Gamma_{\text{electron}} = +2.22$ and $\Gamma_{\text{phonon}} = +2.25$ obtained[47] for pure Pd for temperatures $\gtrsim 3$ K. The presence of conduction electrons masks the influence of TLS on either the specific-heat or thermal-expansion coefficient, and prevents a definitive discussion of TLS in PdSiCu.

D. Disordered crystals

The crystalline fast-ion conductor Na β-alumina has been shown[48–51] to harbor TLS. The TLS reside in the two-dimensional conducting planes, and arise through a stoichiometric excess of Na in these planes. Furthermore, the ionic motion associated with the TLS is constrained to the conducting plane; no Na motion is observed along the crystalline c axis.[50] The thermal expansion of Na β-alumina, the circles of Fig. 10, was measured perpendicular to the c axis. The expansion coefficient (for $T \gtrsim 0.8$ K) is small relative to that of the amorphous dielectric solids in Figs. 2, 4, and 6.

Cubic zirconia, i.e., ZrO_2 stabilized in the cubic phase through the addition of Y_2O_3, is a three-dimensional fast-ion conductor. A sintered sample of this material was found previously to have characteristic glassy properties at low temperatures.[52] The thermal-expansion coefficient of a single-crystal sample, Fig. 10, is close to that[53] of Na β-alumina for temperatures below 2 K.

E. General remarks

All of the disordered, nonmetallic samples show unusual behavior in thermal expansion at temperatures $\lesssim 1$ K. As argued above, this behavior most likely arises from the same low-energy excitations, the TLS that are responsible for the specific-heat anomaly in glasses at $T \lesssim 1$ K. In discussing the specific heat, it has become conventional for authors to fit the data with the approximation $C = aT + bT^3$ even though C is not strictly linear in T at very low temperatures, and in spite of the fact that a T^3 dependence is not observed in the specific heat of any glassy solid in any temperature range for $T < 10$ K. Nevertheless, the fit does permit the rapid comparison of different materials. When used for data obtained at $T \lesssim 1$ K, the coefficient a reflects the magnitude of the TLS contribution, while the coefficient b reflects contributions from phonons and other excitations having energies $\gtrsim 1$ K. The same justification can be applied to thermal-expansion data in use of the fit $\alpha = cT + dT^3$. Figures 12 and 13 show C/T and α/T plotted[25,26,30–32,37,38] as a function of T^2. The coefficients a, b, c, and d, obtained from the straight lines, are listed in Table I. Through Eq. (1), Grüneisen parameters Γ_1 and Γ_3 may be computed individually for the linear and cubic terms. The results of this computation are also presented in Table I.

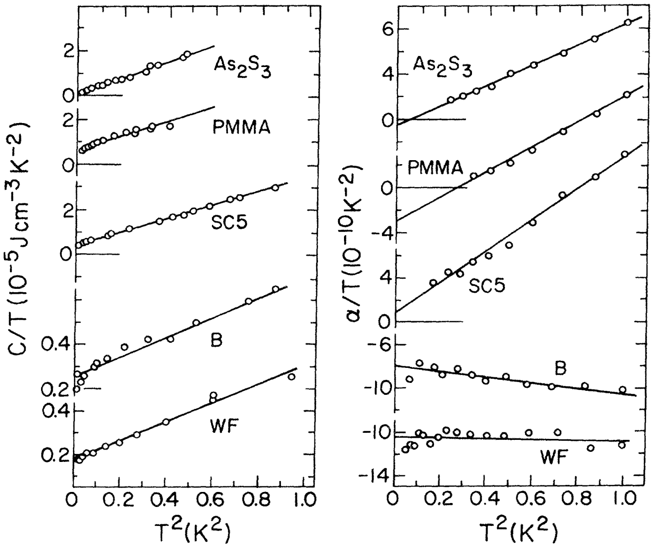

FIG. 12. Specific heats and expansion coefficients of five amorphous solids, divided by T and plotted vs T^2. Spectrosil B and WF have C/T scales expanded by a factor of 10. Sources for the specific-heat data are listed under Refs. 25, 26, and 30–32.

The results of Table I serve to reemphasize the fact that α and Γ are very different for different glassy solids and disordered crystals, with Γ being either large or small, positive or negative. Hence, thermal expansion is the first thermal or transport property that has been measured at $T \lesssim 1$ K and found not to exhibit universal behavior for nearly all amorphous solids. Yet the expansion for $T \lesssim 1$ K is clearly influenced (in some cases dominated) by the TLS.

A second fact displayed by Table I is that the measured Γ are very small relative to the magnitudes deduced in Eq. (7) from ultrasonic data, assuming the deformation potential D were a constant. This observation has been noted previously.[16]

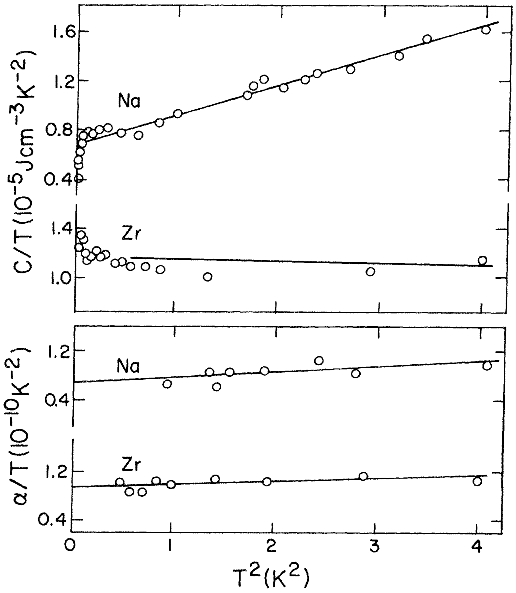

FIG. 13. Specific heats and expansion coefficients of the two crystalline fast-ion conductors Na β-alumina and ZrO_2:Y_2O_3, divided by T and plotted vs T^2. Sources for the specific-heat data are listed under Refs. 37 and 38.

TABLE I. Grüneisen parameters for disordered solids obtained from the linear (Γ_1) and cubic (Γ_3) terms if the specific-heat and thermal-expansion data are fitted by the temperature dependence $C/T=a+bT^2$ and $\alpha/T=c+dT^2$ as in Figs. 12 and 13. Elastic bulk modulus B was obtained from ultrasonic data found in Refs. 25, 26, 30–32, 37, and 38.

Sample	B (10^4 J/cm^3)	a (10^{-5} J/cm^3 K^2)	b (10^{-5} J/cm^3 K^4)	c (10^{-10} K^{-2})	d (10^{-10} K^{-4})	Γ_1	Γ_3
Spectrosil WF	3.5	0.17	0.44	−10.5	−0.5	−65	−1
Spectrosil B	3.5	0.25	0.46	−8.0	−2.5	−34	−6
Spectrosil B (irradiated)[a]						−34	
PMMA	0.82	0.67	3.0	−3.0	+11	−1	+1
As_2S_3	1.4	0.10	3.6	−0.5	+9.0	−2	+1
Glassy PdSiCu						$-\vert \lesssim 0.6 \vert$[b]	
Epoxy SC5	0.75	0.42	2.9	+0.8	+14	+0.4	+1
Crystalline Na β-alumina	27	0.68	0.24	+0.7	+0.07	+8	+2
Crystalline ZrO_2:Y_2O_3	29	1.15		+0.95		+7	

[a] Based on the similarity to a and C of Spectrosil B for $T<2$ K.

[b] An upper limit on $|\Gamma_1|$ for TLS obtained from the slight negative excursion from the straight (dotted) line in Fig. 9 at temperatures $T^2<3$ K^2 assuming that, at $T^2>3$ K^2, Γ_1 is dominated by conduction electrons.

Both anomalies, the nonuniversal character of Γ and the small magnitude of Γ, can be explained readily if the deformation potential D is *different* at different TLS sites. The site i would thus be characterized by a deformation potential D_i as well as by an energy splitting E_i. The density of TLS, per unit interval of E and of D, might then appear schematically as in Fig. 14. The ultrasonic measurements are sensitive to D_i^2 averaged over all TLS. This quantity is represented by $D_{\rm rms}(E)$ in Fig. 14, and depicts the energy dependence postulated to explain ultrasonic results.[15] The thermal-expansion coefficient is sensitive to D_i averaged over all TLS. This quantity is represented by $D_{\rm avg}(E)$ in Fig. 14. A distribution in D has also been used to explain the null effect on ultrasonic attenuation with the application of time-independent stress.[54] It has been suggested[13] that the distribution in D might arise through the postulated[55] local strains present in glassy materials.

Although Fig. 14 does not constitute a proof, it can be seen how $D_{\rm avg}(E)$ could be much smaller than $D_{\rm rms}(E)$, how $D_{\rm avg}(E)$ could be positive as for epoxy SC5 or negative as for SiO_2, and how $D_{\rm avg}(E)$ could have a stronger E dependence than $D_{\rm rms}(E)$. The stronger energy dependence would be reflected in the temperature dependence observed in Γ, as for vitreous silica in Fig. 3.

If the speculation is true that a spectrum of D occurs in disordered solids, then the above discussion assuming D and M are constants must be modified. For vitreous silica the shape of the spectrum (Fig. 14) for intrinsic TLS must be similar to that for the TLS associated with the OH. Otherwise the ratio $D_{\rm OH}/D_{\rm int}$ would probably not have the same magnitude as $(M_{\rm OH}^2)^{1/2}/(M_{\rm int}^2)^{1/2}$. On the other hand, the failure for such ratios to agree, as discussed for SiO_2:K_2O or As_2S_3, could simply indicate that TLS associated with K_2O have a different distribution over D than do the intrinsic TLS, and that the TLS in As_2S_3 have a different spectrum in D than do the TLS in SiO_2.

The difficulty in obtaining a large Γ from the potential of Fig. 1 was discussed in Sec. II. The fact that Γ is small in most of the samples reported here does not eliminate the basic problem. The theoretical computations must eventually yield the very large couplings between TLS and

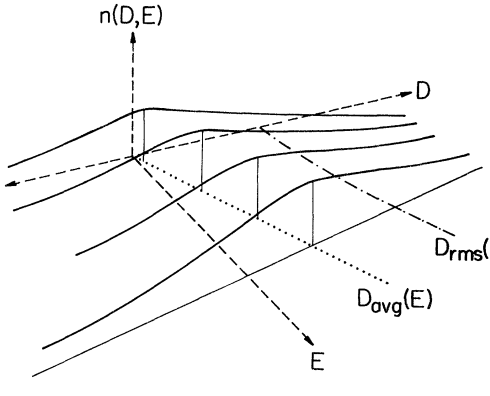

FIG. 14. Schematic drawing showing the distribution $n(D,E)$ of TLS's having energy splitting E and deformation potential D.

strain measured in ultrasonic measurements and depicted as $D_{\rm rms}(E)$ in Fig. 14.

The present work illustrates again the inherent complexity of the phenomenological model based on TLS. Not only do the TLS require a broad spectrum of energies E_i to explain the specific heat, but also a broad spectrum of deformation potentials[14] D_i and M_i to explain the ultrasonic attenuation and thermal expansion. The distribution in deformation potentials would produce a broad spectrum of TLS relaxation times τ_i. A spectrum in τ_i has previously been deduced from resonance measurements,[17] ultrasonic measurements,[56] and specific-heat measurements.[57] These general comments are made without recourse to the assumption that TLS arise from quantum-mechanical tunneling.

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