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Low-Temperature Thermal Expansion of Amorphous Solids

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For most glassy materials at temperatures below ≈1 K, the magnitudes and temperature dependences of specific heat, thermal conductivity, and ultrasonic dispersion are qualitatively similar, independent of chemical composition. It has been suggested that thermal expansion also exhibits this universal behavior. However, from measurements made on amorphous SiO_2, As_2S_3, and two glassy polymers at $T < 1$ K, it is found that the linear expansion coefficient can be positive, negative, large, or small.

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The universal behavior of amorphous solids at temperatures $T \lesssim 1$ K has attracted much attention over the past ten years.[1] For nearly all glassy materials the specific heat is roughly linear in temperature and of the same magnitude independent of chemical composition. This is very different from the $(T/\theta_D)^3$ dependence observed in pure crystals, for which θ_D is the Debye temperature. Also the thermal conductivity and ultrasonic dispersion are similiar among glassy solids, but very different from crystalline solids. This universal low-temperature behavior in amorphous materials is caused by a broad spectrum of localized excitations having a nearly energy-independent density of states. Each excitation would appear to have a ground state and one excited state well separated from other states of higher energy, hence the name two-level states (TLS). A phenomenological model[2,3] suggests that the TLS arise from the tunneling of some entity between two neighboring potential-energy wells.

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 on the observation that, in crystals containing impurities, the expansion coefficient may be very large if the impurity can reorient by tunneling.[5] In a discussion of thermal expansion, it is convenient to use the Grüneisen parameter[6] Γ defined as $\Gamma = 3B\alpha/C$, where B is an elastic modulus, α is the linear thermal expansion coefficient, and C is the specific heat. For phonons $\Gamma \approx 1$, while for crystalline impurities with associated tunneling states, Γ may be as large as 300, and either positive or negative.[5] Indeed, measurements of thermal expansion in amorphous solids[4,7,8] appear to indicate a universal behavior, as for specific heat, with a Γ which is large and negative, $\Gamma \approx -20$. However, those measurements were made only at $T > 1$ K. It is primarily at lower temperatures that the TLS make the strongest contribution to thermal properties. We therefore have measured the thermal expansion coefficients of four glassy solids to temperatures below 1 K. We find that, contrary to expectation, there is not a universal behavior for the thermal expansion coefficient.

Our dilatometer[9] uses a SQUID circuit as a position-sensitive detector to monitor the periodic length changes of a sample caused by an imposed square-wave temperature modulation. The resolution is 2×10^{-4} Å. Samples of ≈3 cm length were cut from vitreous silica[10] (SiO_2), amorphous As_2S_3,[11] polymethylmethacrylate[12] (PMMA), and an epoxy[13] (SC5). The low-temperature limit for each sample was determined by a length change of five times the resolution for a temperature modulation of 10%. The accuracy of a measured expansion coefficient is believed to be ≈±10% as determined by measurements on high-purity copper.

The expansion data are displayed in Figs. 1 and 2 where $\alpha(T)$ has been divided by T^3 to emphasize any departure from the T^3 dependence contributed by phonons, a source of low-temperature thermal expansion other than TLS. Also shown are data from previous measurements on these materials at $T > 1$ K. Below 1 K the $\alpha(T)$ of SiO_2 is large, negative, and proportional to T as predicted by the earlier measurements.[14] On the other hand, the $\alpha(T)$ of SC5, PMMA, and As_2S_3 are small and positive over the available temperature range. The empirical Grüneisen parameters[10-13] are plotted in Fig. 3, where the vertical scale for SiO_2 has been *compressed* by a factor of 10. Also shown are the direct measurements[15] of Γ for SiO_2. In the direct measurement one observes a temperature change resulting from an imposed change in length instead of observing the length change caused by an imposed change in temperature as in the present measurements.

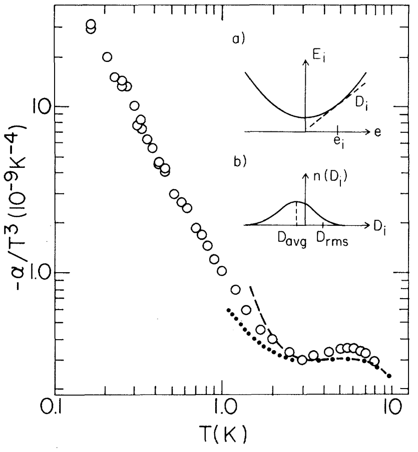

FIG. 1. The *negative* linear thermal expansion coefficient α of vitreous silica, divided by T^3 to emphasize departure from a T^3 phonon contribution. The data from two independent sets of measurements are indistinguishable. Dashed line, data of Ref. 4. Dotted line, data of Ref. 7. Insets: (a) Possible effect of local strain e on energy E_i of a TLS. (b) Speculated distribution of strain-coupling coefficients D_i.

The specific heats C of amorphous solids may be fitted[1] by the expression $C = c_1T + c_3T^3$ for $0.1 < T < 1$ K. The first term, which dominates C at $T < 1$ K, is attributed to the TLS. The thermal expansion of SiO_2 also can be fitted by $\alpha = a_1T + a_3T^3$. If this fit is applied to all samples at $T < 1$ K, and if the linear term is assumed to be contributed by TLS, we obtain for the TLS Grüneisen parameter $3Ba_1/c_1$ values of roughly -30, -1, -0.4, and $+0.3$ for SiO_2, PMMA, As_2S_3, and SC5, respectively.[16] Thus it is clear from these results and Figs. 1–3 that the expansion coefficients, or the Grüneisen parameters, of glassy solids do not obey a universal behavior at low temperatures.

The commonly used theory[2,3] for TLS is phenomenological and, as such, permits one to correlate the results of different measurements. In particular, ultrasonic attenuation measurements may be compared with the present thermal-expansion results. The energy E of each TLS is changed slightly by the stress of an ultrasonic wave, thus altering the statistical probability that the excited states are populated. This process of thermal relaxation causes an attenuation of the ultrasonic wave. To be more specific, the change in energy E_i at TLS site i is $\partial \ln E_i/\partial \ln V \equiv D_i/E_i$. The quantity D_i has generally been treated as a constant in the literature, in which case the ultrasonic attenuation[17,18] is proportional to D^2 with $|D| \approx 1$ eV. The Grüneisen parameter may be defined[6] as $\Gamma = \sum_i \Gamma_i C_i/\sum_i C_i$, where the sum is over all TLS sites and $\Gamma_i = -\partial \ln E_i/\partial \ln V = D_i/E_i$. Again assuming that D is a constant and using the magnitude determined from ultrasonic measurements, we have $|\Gamma| = (D\sum_i C_i/E_i)/\sum_i C_i \approx 10^4/T$. Hence at $T = 1$ K, $|\Gamma| \approx 10^4$. This may be contrasted with the weaker temperature dependences of the measured Γ in Fig. 3 and with the much smaller measured magnitudes, namely, $|\Gamma| < 15$ at 1 K. In brief, the coupling of individual TLS to strain fields (measured ultrasonically) indicates a much larger thermal expansion coefficient than is observed. A cancellation of the contributions of individual TLS to thermal expansion must occur as has been discussed

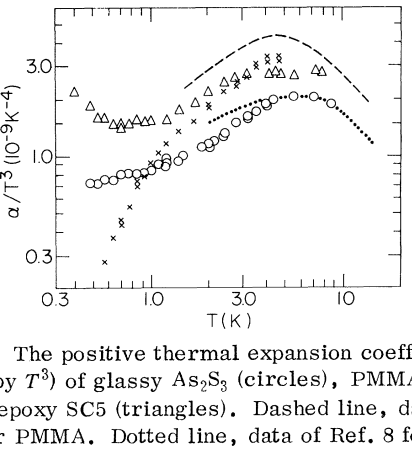

FIG. 2. The positive thermal expansion coefficient α (divided by T^3) of glassy As_2S_3 (circles), PMMA (crosses), and epoxy SC5 (triangles). Dashed line, data of Ref. 7 for PMMA. Dotted line, data of Ref. 8 for As_2S_3. The specific heats of these materials are of the same magnitude, but a factor of $\gtrsim 2$ larger than for vitreous silica.

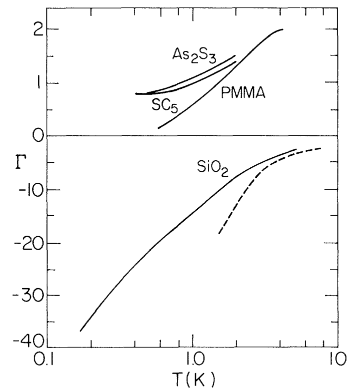

FIG. 3. The empirical Grüneisen parameters Γ for glassy As_2S_3, PMMA, SC5, and, on a scale *compressed* by a factor of 10, vitreous SiO_2. Dashed line, direct measurement of Γ for SiO_2 from Ref. 15.

previously.[19]

A cancellation could occur if the D_i were a function of the energy E_i at TLS site i. Then $D_{\rm rms} = (\langle D_i^2 \rangle)^{1/2}$ is a quantity more appropriate to ultrasonic attenuation, since the relaxation process is independent of whether E_i increases or decreases with application of stress. For thermal expansion $D_{\rm av} = \langle D_i \rangle$ is a more appropriate quantity, as the individual signs are now important in determining whether the sample expands or contracts. The energy dependence of $D_{\rm rms}$ must be weak, or the temperature dependence of the computed ultrasonic attenuation would not agree with observation.[17,18,20,21] On the other hand, $D_{\rm av}$ must have a linear energy dependence to give a temperature-independent Γ, or a dependence of $\approx E^{1/2}$ to give $\Gamma(T)$ roughly proportional to $T^{-1/2}$ as observed for vitrious silica (Fig. 3). An illustration of how $D_{\rm rms}$ might differ from $D_{\rm av}$ is provided by the inset in Fig. 1. The energy E_i at site i may be perturbed by local strain[22] e as in Fig. 1(a). The slope of the E_i vs e curve at strain e_i is just D_i. A spectrum of local strains e_i would create a spectrum of D_i. For convenience we take the distribution of the D_i to be a Gaussian lying slightly off center as shown in Fig. 1(b). If the distribution $n(D_i)$ should shift slightly as a function of E (or temperature or material), a large fractional change would occur for $D_{\rm av}$ but not for $D_{\rm rms}$.

In summary, we have observed that the thermal expansion coefficients of amorphous solids do not follow the universal behavior observed for specific heat, thermal conductivity, and ultrasonic dispersion. It would appear that a distribution of strain-coupling coefficients D_i must be added to the broad distributions over energies and over relaxation times which are believed to exist for the TLS.

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