Low-temperature thermal expansion of glassy solids

A. C. Anderson
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801
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A summary is presented of thermal-expansion measurements on disordered solids at temperatures $T \lesssim 1$ K, where two-level states dominate or influence most properties. The expansion coefficients are in quantitative agreement with the tunneling model of two-level states.

Localized excitations in amorphous solids, and in certain disordered crystals give rise at temperatures $T \lesssim 1$ K to a specific heat C which is roughly linear in T and a thermal conductivity κ, roughly proportional to T^2. The magnitudes of C and, especially, κ are approximately the same for various materials.[1] It was initially speculated that the thermal-expansion coefficient α, likewise would be an anomalous, universal property of glasses with α being large and negative.[2] These speculations, however, were based on data obtained at $T > 1$ K. When expansion measurements were extended below 1 K, such a universal behavior was not found.[2] What has been observed is the subject of this report.

As a normalized expansion coefficient, it is convenient to use the Grüneisen parameter defined as $\Gamma = 3\alpha B/C = \sum_i \Gamma_i C_i / \sum_i C_i$. Here B is the elastic bulk modulus and Γ_i and C_i are the contributions from excitation i. The experimental data at $T \lesssim 1$ K may be fitted in the conventional manner,[3] i.e., $\alpha = aT + bT^3$ and $C = cT + dT^3$, where the terms linear in T are related to the localized excitations generally identified as two-level states (TLS). A Grüneisen parameter appropriate to the TLS is therefore $\Gamma_{TLS} = 3aB/c$. Measured values of Γ_{TLS} for several materials[2,4–6] are summarized in Table I. Clearly a universal behavior is not evident, and a statement like[7] "as a rule, Γ_{TLS} is negative, and the absolute values of Γ_{TLS} are very large, i.e., of the order 10^2," does not receive support from the experimental results. Rather, Γ_{TLS} can be either positive or negative, and can be as small in magnitude as the value $\Gamma \approx 1$, typically found for thermal phonons and conduction electrons.

TABLE I. Grüneisen parameters Γ_{TLS} attributed to two-level states. The $(KBr)_{0.5}(KCN)_{0.5}$, Na β-alumina, and ZrO_2:Y_2O_3 are crystalline solids having the same properties as amorphous solids at $T \lesssim 1$ K.

Material (amorphous solids)	Refs.	Γ_{TLS}
SiO_2	2	$-(34-65)$
SiO_2:K_2O	5	-4
PMMA	2	-1
As_2S_3	2	-2
Pd-Si-Cu	2	$-\lvert\lesssim 0.6\rvert$
Epoxy SC5	2	$+0.4$
Teflon[a]	4	$\lesssim\lvert 1\rvert$
(crystalline orientational glass)		
$(KBr)_{0.5}(KCN)_{0.5}$	6	$+1$
(crystalline fast-ion conductors)		
Na β-alumina	2	$+8$
ZrO_2:Y_2O_3	2	$+7$

[a]The Teflon sample was $\approx 60\%$ crystalline. Therefore, Γ_{TLS} for the amorphous portion alone would be $\lesssim\lvert 2\rvert$.

A phenomenological model for the TLS assumes some entity tunnels between two neighboring potential-energy wells. This tunneling produces a ground-state manifold having two levels separated by an energy $E = (\Delta^2 + \Delta_0^2)^{1/2}$, where Δ is the asymmetry of the two wells and Δ_0 is the energy splitting caused by tunneling.[1] The coupling of a TLS to a strain field e is represented by a deformation potential,

$$D = dE/de = (\Delta/E)\partial\Delta/\partial e + (\Delta_0/E)\partial\Delta_0/\partial e. \quad (1)$$

The second term is generally believed to be small, and so $D = (\Delta/E)\partial\Delta/\partial e = (\Delta/E)\gamma$, where γ is a constant.[1,8,9]

It is assumed that each TLS can have different values of the independent parameters Δ and Δ_0, and so for the sample as a whole there is a distribution over Δ and Δ_0. The distribution $n(\Delta)$ within the energy range of interest (i.e., $E \lesssim 1$ K) is assumed to be constant, $n(\Delta) = n_0$, with Δ ranging over both positive and negative values[8] so that the averaged quantity $\langle\Delta\rangle = 0$. A more complicated distribution is assumed for Δ_0. These distributions in Δ and Δ_0 predict dispersions, in both the ultrasonic and dielectric response, which are in remarkable agreement with experiment over a factor of $\approx 10^{12}$ range in frequency.[1,10]

The expansion data of Table I provide another test of the form of $n(\Delta)$ assumed in the tunneling model. A Γ_{TLS} can be obtained readily from the tunneling model[1] by recalling that, for a two-level state, C_i is a Schottky peak centered near $T \approx E_i$. Therefore, since only TLS having $E \approx T$ need be considered, and since $\Gamma_i = \partial(\ln E_i)/\partial e = D_i/E_i$,

$$\Gamma_{TLS} = \sum_i \Gamma_i C_i / \sum_i C_i \approx \langle\Gamma_E\rangle \approx \langle D_E\rangle/E \approx \langle\Delta_E\rangle\gamma/E^2. \quad (2)$$

Both Γ_{TLS} and γ have been measured. From ultrasonic measurements[1] it is known that $\gamma/E \gtrsim 10^3-10^4$ for $E \approx T \lesssim 1$ K and, from Table I, that $\lvert\Gamma_{TLS}\rvert \approx 0.5-50$. Therefore, using Eq. (2), one obtains $\lvert\langle\Delta_E\rangle/E\rvert \lesssim 10^{-2}$ for those glassy materials that have been measured. For vitreous silica explicitly,[11] $\lvert\langle\Delta_E\rangle/E\rvert \lesssim 5\times 10^{-3}$ and, for polymethylmethacrylate or epoxy,[12] $\lvert\langle\Delta_E\rangle/E\rvert \lesssim 5\times 10^{-4}$.

As noted above, the tunneling model assumes $n(\Delta)$ is constant for Δ both positive and negative, so the quantity $\langle \Delta \rangle$ is zero. Because Δ and Δ_0 are taken as independent parameters, this assumption about $n(\Delta)$ also gives $\langle \Delta_E \rangle / E = 0$. By contrast, since Δ can be as large as E, an *asymmetric* distribution could give an average as large as $|\langle \Delta_E \rangle / E| = 1$. Therefore, the experimental result that $|\langle \Delta_E \rangle / E| \approx 10^{-3}$ is consistent with a symmetric $n(\Delta)$ and is in excellent agreement with the tunneling model as originally formulated.[13] The small Γ_{TLS} that is observed (see Table I) could arise from a slight asymmetry in $n(\Delta)$, or from the term[14] $(\Delta_0/E)\partial\Delta_0/\partial e$ in Eq. (1) which heretofore has been assumed to be negligible.

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[1]For a review of the subject, see *Amorphous Solids*, edited by W. A. Phillips (Springer, Berlin, 1981).

[2]D. A. Ackerman, A. C. Anderson, E. J. Cotts, J. N. Dobbs, W. M. MacDonald, and F. J. Walker, Phys. Rev. B **29**, 966 (1984), and references therein.

[3]It is not essential to assume a term linear in T. The limit of $3\alpha B/C$, as T becomes small, would give essentially the same value for Γ_{TLS}.

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[5]W. M. MacDonald, A. C. Anderson, and J. Schroeder, Phys. Rev. B **31**, 1090 (1985).

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[7]Yu. M. Galperin, V. L. Gurevich, and D. A. Parshin, Phys. Rev. B **32**, 6873 (1985).

[8]W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

[9]A. C. Anderson, J. Non-Cryst. Solids (to be published).

[10]See, for example, S. Hunklinger, in *Phonon Scattering in Condensed Matter*, edited by W. Eisenmenger, K. Lassmann, and S. Dottinger (Springer, Berlin, 1984), p. 378.

[11]J. E. Graebner, L. C. Allen, B. Golding, and A. B. Kane, Phys. Rev. B **27**, 3697 (1983).

[12]P. Doussineau and W. Schon, J. Phys. (Paris) **44**, 397 (1983).

[13]The model as originally formulated appears not to be in quantitative agreement with all experimental data obtained for certain glasses. See Refs. 5 and 10.

[14]W. A. Phillips, J. Low Temp. Phys. **11**, 757 (1973).