

Experimental Evidence on Time-Dependent Specific Heat in Vitreous Silica

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Measurements have been made of the heat capacity of thin plates of vitreous silica between 0.35 and 1.6 K. In an adiabatic sample arrangement the time-resolved specific heat was measured over a time scale from 2 μ sec to 0.5 msec. The observed time dependence of the heat capacity is in quite good agreement with the tunneling model, which predicts a logarithmic increase in time. In addition, a much stronger time dependence was observed above 1 K, which was interpreted as a decoupling of excess modes from the Debye phonons.

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At very low temperatures, $25 \text{ mK} \leq T \leq 2 \text{ K}$, the temperature dependence of the specific heat of amorphous SiO_2 is of the form^{1,2}

$$C_p = C_1 + C_D + C_{\text{excess}} \\ = a_1 T^{1+n} + a_3 T^3 + a_{\text{excess}} T^3 + \dots, \quad (1)$$

where the first term ($n = 0.3-0.5$) arose from low-energy excitations intrinsic to the amorphous state and the cubic T term C_{excess} is observed. It has been suggested³ that the roughly linear T term is a result of two-level tunneling states. One of the consequences of the tunneling model is that the specific heat should be a function of the time scale of the experiment. Because of the wide range of tunneling probabilities in two-level systems, the relaxation time τ varies widely for the different states and the two-level systems may be decoupled from the phonon specific heat for experimental times $t < \tau$. The tunneling model predicts⁴ that the linear term of the specific heat decreases logarithmically with experimental time t .

In the past a number of heat-pulse experiments have been performed⁵⁻⁷ to observe time-dependent specific heat in silica glasses. All these experiments were arranged for one-dimensional heat-flow diffusion, and the temperature profiles were analyzed with the phenomenological heat-diffusion theory. In some of these experiments a slight increase of the thermal diffusivity α was observed, which has been interpreted as a time-dependent specific heat.^{5,7} In similar measurements we have found evidence⁸ that the thermal conductivity K is time dependent and as a consequence the relation $C_p = K/\alpha$ does not hold.

Because of these obvious complications we have designed a nearly adiabatic sample arrangement to observe the time-dependent specific heat directly. For a vitreous silica sample of thickness

$d = 50 \mu\text{m}$ and diffusivity⁸ $\alpha \approx 20 \text{ cm}^2/\text{sec}$ one can calculate a diffusion time $\tau_d \approx d^2/2\alpha \approx 1 \mu\text{sec}$.

After heating the sample the relaxation to the temperature bath T_0 will be determined by heat diffusion parallel to the surface. By assuming a surface heater and a point-contact thermometer with a diffusion distance $L = 3 \text{ mm}$ to the temperature bath, the thermometer area is nearly adiabatic up to times $\tau_L \approx L^2/10\alpha \approx 0.5 \text{ msec}$. Thus, the time dependence of the sample temperature under adiabatic conditions can be observed between 1 and 500 μsec .

In a recalculation of the tunneling model, Black⁹ has calculated the temperature decay $\vartheta(t)$ in an adiabatic heat-pulse experiment (for long but not infinite time). Black has shown that the density of states for the two-level systems determined from ultrasonic measurements are inconsistent with long-time specific-heat measurements (at $t = t_{\text{max}}$), and therefore he artificially introduced anomalous levels. In order to fit our time-dependent specific-heat data we assumed that the linear term in Eq. (1) varies logarithmically with time and, in addition, differences in the specific heat are explained by C_{excess} :

$$\vartheta(t) = \frac{Q}{V} \left[\rho C_D + \rho C_{\text{excess}} + a_1 T^1 \frac{\ln(4t/\tau_{\text{min}})}{\ln(4t_{\text{max}}/\tau_{\text{min}})} \right]^{-1}, \quad (2)$$

where $\tau_{\text{min}} = 0.5 \times 10^{-9} T^{-3} \text{ sec}$ is the shortest relaxation time in the dominant phonon approximation,⁹ Q/V is the quantity of heat per volume, and ρ is the density.

Details of our experimental arrangement are shown in the inset of Fig. 1. A disk-shaped sample of Suprasil I with 12 mm diameter and 70 μm thickness was mounted on a copper block. One surface of the sample has been evaporated with a $7.4 \times 9.2 \text{ mm}^2$ -wide gold-film heater of about 50

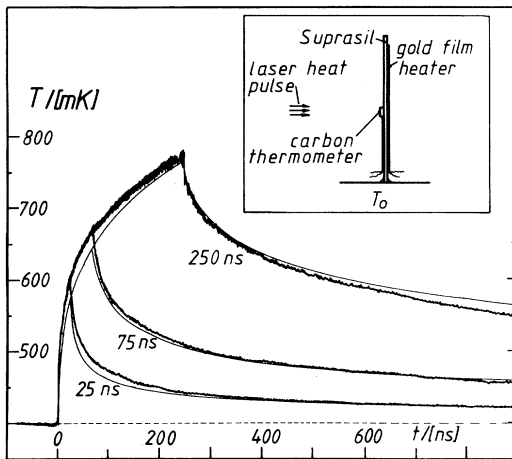


FIG. 1. Surface temperatures $T(t)$ obtained by heating with different laser pulses of width t_p . The straight lines are calculated from diffusion theory, Eq. (3). The inset shows the experimental arrangement (see text).

nm thickness. On the other side a $1.8 \times 1.8 \text{ mm}^2$ -wide carbon thermometer (thickness $\sim 1 \mu\text{m}$) has been attached. This has been done by rubbing or-

dinary pencil material onto the $\sim 1\text{-}\mu\text{m}$ rough surface of the sample and contacting with gold thin film evaporated in a meandering pattern. The carbon thermometer has a resistance of about $1 \text{ k}\Omega$ at 0.4 K and shows a temperature characteristic similar to a Speer resistor. The sensitivity of the carbon thermometer was calibrated against a Ge-resistor thermometer. With the acceptance of a power dissipation in the carbon resistor of about 10 nW and with use of a $50\text{-}\Omega$ termination, a sensitivity of $\sim 500 \mu\text{V/K}$ was available. Thus, a stationary temperature gradient in the sample of $\sim 3 \text{ mK}$ and a minimum temperature resolution of $\sim 0.2 \text{ mK}$ were obtained. The temperature resolution was achieved by a boxcar averager, but was limited by the temperature stability of our ^3He cryostat and the repetition rate (10 sec^{-1}) of the experiment.

In order to test the response time of the carbon thermometer we applied a laser heat pulse t_p to the carbon resistor area (Fig. 1). The resulting surface-temperature profiles are compared with theoretical curves calculated from diffusion the-

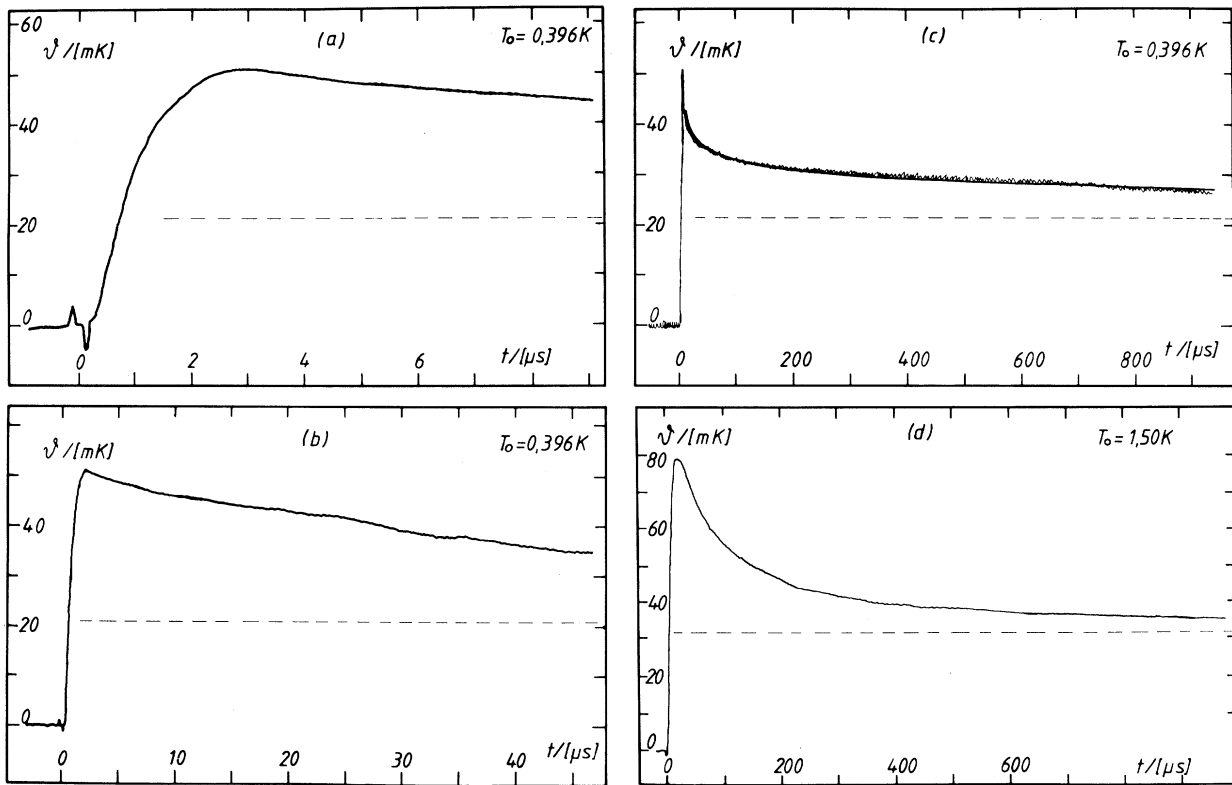


FIG. 2. Temperature profiles $\Delta(t)$ for the $70\text{-}\mu\text{m}$ sample. The dashed lines represent the temperature rise expected from long-time data $C_p(t=1 \text{ sec})$; the solid line in (c) is calculated by Eq. (2). Profile (d) shows the unexpected strong nonlogarithmical decay observable around 1 K .

ory:

$$T(t) = \frac{t^{1/2} - (t - t_p)^{1/2} \Theta(t - t_p)}{C_p(T, t) \alpha^{1/2}}, \quad (3)$$

where $\Theta(t - t_p)$ is the Heaviside function and $C_p(T, t)$ was calculated by iteration according to Eq. (2). The response time of the carbon thermometer is shorter than 5 nsec, and the heat transport from the surface to the bulk is clearly diffusive even in a nanosecond time scale.

With application of electrical pulses of duration $t_p = 50$ nsec to 5 μ sec to the gold thin film, the resistive heating produces a diffusive heat transport through the sample. The resulting temperature profiles $\vartheta(t)$ are shown in Fig. 2. At shorter times [Fig. 2(a)], a diffusive increase of the signal is observed. After the heat diffusion ($t \geq 3$ μ sec), the phonon system of the sample approaches equilibrium and a logarithmic decay [Figs. 2(b) and 2(c)] of the temperature is observed, which is interpreted as due to the coupling of two-level systems. In Fig. 2(d), an unexpected non-logarithmical, but nearly exponential, temperature decay has been measured. This effect was clearly seen above 1 K, but also down to the lowest temperature an exponential contribution to the temperature decay has been observed, which is superimposed on the logarithmic part. For $T \geq 2$ K, the overshoot of $\vartheta(t)$ is masked by heat-diffusion transport, because of smaller α values, and in the adiabatic time scale $\tau_d < t < \tau_L$, $\vartheta(t) \approx \text{const}$ was observed.

In a series of experiments we have measured two samples of thicknesses 70 μ m ($\tau_L \approx 0.5$ msec) and 48 μ m (with slightly reduced geometries $\tau_L \approx 0.2$ msec) in a temperature range 0.366–1.50 K. The results are shown in Fig. 3 in terms C_p/T^3 vs $\ln t$, in order to compare them with theory. According to Eq. (2), the specific heat decreases linearly with $\ln t$, which is shown by the dotted lines (fitting to the long-time heat capacity of Suprasil). In addition, the contribution of the two-level systems only has been shown by neglecting C_{excess} in Eq. (2) for temperatures $T \leq 0.715$ K. At these temperatures, our time-dependent specific-heat data are in good agreement with Eq. (2) (dashed lines, $C_{\text{excess}} = 0$), but only for times $t \leq 20$ μ sec. For longer times the data increase stronger than logarithmically, and for times $t \leq 200$ μ sec a good fit to Eq. (2) is observed.

Very recently, Loponen *et al.*¹⁰ reported on the observation of time-dependent specific heat in a Suprasil W sample of thickness 210 μ m. Over times ranging from 30 μ sec to a few milliseconds

they observed a decay of the sample temperature, which has been qualitatively interpreted as the coupling of the tunneling states to the phonon system. In Fig. 4, the short-time heat-capacity data of Loponen *et al.* are shown together with our data for two experimental times, and with long-time heat-capacity data.^{1,2,8} Below 0.5 K, both experiments show a reduction of the specific heat which is of the same order for the corresponding reduction in time. Around 1 K, the 30- μ sec-time-scale experiment on Suprasil W shows a reduction to $0.8 \times C_p$ (1 sec), whereas in our 3- μ sec-time-scale experiment on Suprasil a reduction to $0.3 \times C_p$ (1 sec) appears. As Suprasil (~ 1200 ppm OH) and Suprasil W (< 1.5 ppm OH) are different materials,¹ a bump in C_p/T^3 around 1 K is observed for Suprasil W only, implying a new set of excitations.² It may be argued that these excitations behave similarly to those in Suprasil. From our

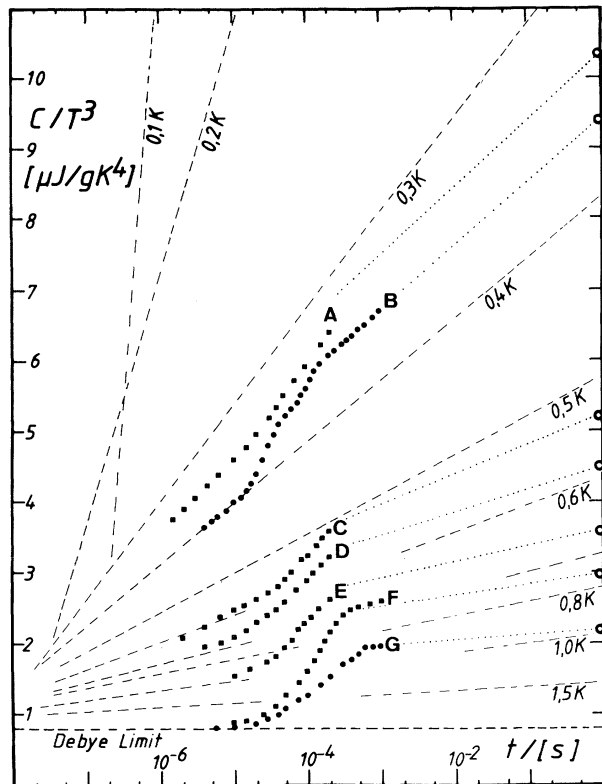


FIG. 3. Time-dependent specific-heat data for $C_p(t)/T^3$ vs $\ln t$: curve A, 366 mK; curve B, 396 mK; curve C, 596 mK; curve D, 715 mK; curve E, 890 mK; curve F, 1.005 K; curve G, 1.50 K; closed circles, 70- μ m sample; closed squares, 48- μ m sample; open circles, long-time data from Refs. 1 and 8. The dotted lines and the dashed ($C_{\text{excess}} = 0$) lines are according to Eq. (2).

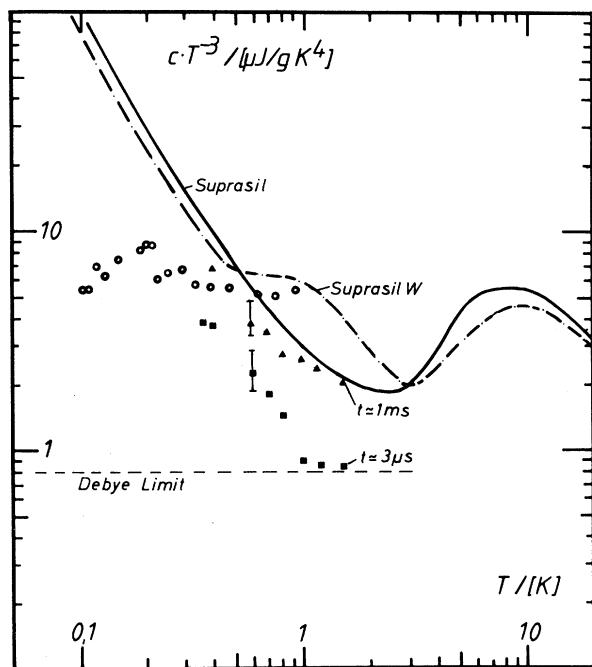


FIG. 4. Long-time and short-time heat capacity for vitreous silica, plotted C_p/T^3 vs T . The open circles are results from Loponen *et al.* (Ref. 10), obtained for a 210- μm (Suprasil W) sample on a $\sim 30\text{-}\mu\text{sec}$ time scale. The squares and the triangles are our results from a 48- μm (Suprasil) sample on two different time scales.

experiments one may interpret the decoupling of C_{excess} by the existence of "anomalous" two-level systems with higher energy splittings.⁹ In view of the observed relaxation times of about 100 μsec at 1 K, it is understandable that the excess excitations do not affect the thermal conductivity because of their weak coupling to the phonon sys-

tem.

In summary, we have measured the time-dependent specific heat of vitreous silica samples with thicknesses of 48 and 70 μm in a time range of 1 μsec to 1 msec. From the experimental data it has been shown that the two-level systems with constant density of states decouple logarithmically in time, as supposed by Black.⁹ In addition, the excess specific heat, seen in long-time experiments, decouples with relaxation times τ , $\approx 100 \mu\text{sec}$.

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