

## Low-temperature thermal properties of a sol-gel glass

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The thermal conductivity and specific heat of an uncompacted sol-gel glass have been measured over the temperature range  $T \approx 0.1-10$  K. Relative to the compacted product, vitreous silica, the specific heat attributed to two-level states at  $T \leq 1$  K is larger by a factor of 15, but the thermal conductivity is unchanged even though the phonon velocities are smaller by a factor of 2. At  $T > 1$  K, phonon transport appears to be limited by scattering from pores intrinsic to the sol-gel product.

### I. INTRODUCTION

Glasses prepared by sol-gel processes have been of interest to researchers not only for their possible technological value, but also for their potential to provide information about the nature of glasses and the gel-to-glass conversion.<sup>1</sup> Although a diversity of techniques has been employed to probe the nature of the evolution of the sol-gel glass to the final product, as well as the final product itself, no low-temperature measurements of thermal properties have been reported. A study of the low-energy excitations which exist in a sol-gel product that has not completely evolved to its final state could provide a deeper understanding of these ubiquitous excitations, excitations which are found in nearly all amorphous solids and in some disordered crystals.

Characteristic behavior of glasses and other amorphous materials at temperatures below  $\approx 1$  K includes a linear temperature dependence of the specific heat and a quadratic temperature dependence of the thermal conductivity.<sup>2</sup> A phenomenological model that regards the localized low-energy excitations as resulting from units of molecular dimensions tunneling in double-well potentials accounts for the above-mentioned behavior. According to this two-level state (TLS) model, the linear term in the specific heat is proportional to the density of TLS sites. Thus, specific-heat measurements probe the TLS density,  $n(E)$ , which is found to be essentially a constant over the energy range of at least  $E = 10^{-3}-10$  K. Interaction with the strain fields of phonons allows for thermal equilibration of the TLS. For those TLS of energy  $E$ , there is a broad distribution in equilibration times. This broad distribution in TLS-phonon interactions accounts for the  $T^2$  dependence of the thermal conductivity. Therefore, thermal-conductivity measurements serve to probe the coupling of the TLS to strain fields. According to the TLS model, the specific heat  $C$  and the thermal conductivity  $\kappa$  are of the form<sup>2</sup>

$$C \propto nT, \quad (1)$$

$$\kappa \propto \rho v T^2 / \gamma^2 \bar{P}, \quad (2)$$

where  $v$  here, and throughout this paper, is an appropriately averaged velocity for the three acoustic modes,  $\rho$  is the mass density,  $\gamma$  is the TLS-phonon coupling constant,

and  $\bar{P}$  is the density of TLS interacting most strongly with phonons. Typically,  $n/\bar{P} \approx 10$ .

Additional characteristic features of glasses occur above  $\approx 1$  K. These include a temperature-independent regime or "plateau" in the thermal conductivity and a peak in the quantity  $C/T^3$  near  $T \approx 10$  K. It is not known if the low-energy excitations responsible for this behavior are related to the TLS.

Although vitreous silica has been studied extensively, the localized low-energy excitations in these (or other) glasses have not been identified. Additional information is, therefore, desirable. A study of the sol-gel product is particularly interesting because, after heat treatment, the material is virtually indistinguishable from vitreous silica,<sup>3</sup> yet prior to such treatment the sol-gel product (dubbed sol-gel for the remainder of this paper) is different in many respects.<sup>1</sup> Hence, we have made a comparison between the low-temperature thermal properties of vitreous silica and of sol-gel using measurements of specific heat, thermal conductivity, and phonon velocities.

### II. EXPERIMENTAL TECHNIQUES AND RESULTS

A solution of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  in ethanol was hydrolyzed, using HCl as a catalyst. During initial stages of hydrolysis, the mixture was heated in vacuum to  $70^\circ\text{C}$  to drive off excess ethanol and water. The liquid was then cast into petri dishes, where the formation of the gel occurred. The gel was dried at room temperature. The dishes were covered in order to control the rate of shrinkage of the gel.

The sample obtained by the above process was clear and relatively free of cracks. An immersion technique was used to measure the density, the result being  $\rho = (1.79 \pm 0.02) \times 10^3 \text{ kg/m}^3$ . A scanning electron microscope revealed no features (e.g., pores) down to the 500-Å resolution of the instrument. Indeed, such gel-derived glasses typically have pore sizes of 20–80 Å, with the distribution of pore sizes heavily weighted toward 20 Å diameters.<sup>4,5</sup>

The sample was prepared in 1982 by S. D. Brown and K. S. Mazdiyasi. Thermal-conductivity measurements were made in October, 1984; specific-heat measurements

were performed in June, 1985. Sound-velocity measurements were made in November, 1984 and again in June, 1985. During the period over which the various measurements were taken, the samples were stored in a loosely covered dish at room temperature. As the two sets of sound-velocity measurements were in agreement, no significant further drying of the sample occurred over this period.

The thermal-conductivity sample was a rectangular bar of cross-sectional area,  $a$ . As the bar of sol-gel was short, a two-heater method was used to measure the thermal conductivity. Two heaters, separated by a distance  $D$ , were wound around the bar. A carbon-chip resistance thermometer was placed at one end of the sample, and the other end was thermally attached to a temperature-regulated refrigerator. A known power,  $\dot{Q}$ , was dissipated in one heater; the temperature at the end of the sample was recorded; the same power was then switched to the second heater, and the new temperature was recorded. For a temperature change,  $\Delta T$ , at the end of the sample, the thermal conductivity  $\kappa$  was calculated from the relation  $\kappa = (\dot{Q}/\Delta T)(D/a)$ . The carbon thermometer was calibrated *in situ* against a germanium resistance thermometer. The germanium thermometer had been calibrated to an accuracy better than 1% on the EPT 76 temperature scale against National Bureau of Standards superconducting fixed points, using a cerium-magnesium-nitrate magnetic thermometer for interpolation. The dominant source of error was the  $\approx 4\%$  uncertainty in  $D/a$ . Our measured conductivity for the sol-gel is plotted in Fig. 1 along with similar measurements on vitreous silica for comparison.<sup>6</sup>

A heat-pulse technique was used to measure the specific heat. A known amount of heat,  $Q$ , was pulsed into the sample, and the temperature rise and subsequent decay, detected with a carbon-chip resistance thermometer, were recorded by a signal averager. From the temperature

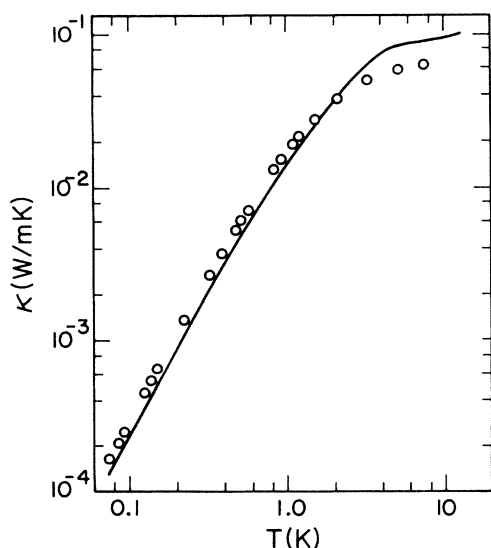


FIG. 1. Thermal conductivities  $\kappa$  versus temperature for a sol-gel glass ( $\circ$ ) and for vitreous silica (solid line, Ref. 6).

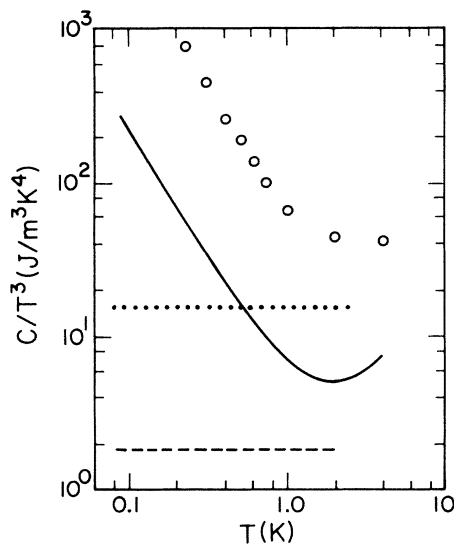


FIG. 2. Specific heats  $C$  divided by  $T^3$ , for sol-gel glass ( $\circ$ ) and vitreous silica (solid line, Ref. 6). The dotted line is the computed Debye phonon contribution for the sol-gel glass; the dashed line is the phonon contribution for the vitreous silica. The density of the sol-gel is  $1.79 \times 10^3 \text{ kg/m}^3$ , that of vitreous silica is  $2.20 \times 10^3 \text{ kg/m}^3$ .

versus time plots, the initial temperature change of the sample was inferred, and the specific heat  $C$  was calculated from the equation,  $C = Q/\Delta TV$ . Here,  $V$  is the volume of the sample as computed from the measured mass and the measured density. The contribution of addenda to the heat capacity was estimated to be  $\leq 1\%$  at 5 K and less at lower temperatures and was, therefore, ignored. The measured specific heat for the sol-gel is shown in Fig. 2, together with earlier data for vitreous silica.<sup>6</sup> In addition, the Debye phonon contributions, computed from the measured sound velocities, are indicated for each sample.

For measurements of sound velocities, two  $1.3 \times 10^7$  Hz quartz transducers were mounted on opposite sides of a polished piece of sol-gel. Three to five echoes could be observed for each applied rf pulse. Both transverse,  $v_T$ , and longitudinal,  $v_L$ , sound velocities were measured by this ultrasonic technique. To obtain a velocity at much higher frequencies,  $\approx 2 \times 10^{10}$  Hz, Brillouin scattering measurements were undertaken for the longitudinal velocity.<sup>7</sup> Over this frequency range of  $10^7$ – $10^{10}$  Hz we could detect no dispersion at room temperature. The measured velocities are listed in Table I. As comparisons will also

TABLE I. Ultrasonic velocities in units of  $10^3$  m/sec. For the Vycor and sol-gel measurements, the uncertainty is  $\approx 5\%$ .

	Longitudinal	Transverse
Vitreous silica	5.8	3.7
Porous Vycor	3.5	2.1
Sol-gel	3.1	1.8

be made with porous Vycor, we measured the ultrasonic velocities for one sample of Vycor. The results, included in Table I, are in good agreement with an earlier measurement.<sup>8</sup>

It will be noted from Table I that the presence of pores in the sol-gel or Vycor results in a factor of  $\approx 2$  reduction of ultrasonic velocity relative to that of solid silica glass. This behavior has been studied in other porous materials<sup>9,10</sup> and is the subject of theoretical investigations.<sup>10,11</sup>

### III. DISCUSSION

We first focus on the behavior observed at  $T \lesssim 1$  K where TLS are the dominant excitations, leaving a discussion of higher-temperature data to later in this section.

The specific heats  $C_{\text{TLS}}$  associated with the TLS alone may be obtained from Fig. 2 by subtracting from the measured specific heats at  $T < 1$  K, that contributed by the phonons as represented by the dashed or dotted lines. It is thereby found that  $C_{\text{TLS}}$  for the sol-gel is a factor of 15 larger than that of vitreous silica. In other words, the drying or compacting process required to produce vitreous silica from the present sol-gel product would decrease the density of states,  $n$ , by a factor of 15. With the larger density of states, it might be expected from Eq. (2) that the thermal conductivity of the sol-gel would be reduced considerably relative to that of vitreous silica. However, in Fig. 1 there is very little change in  $\kappa$  between the two glasses for temperatures below the "plateau" (i.e.,  $T \lesssim 1$  K). This appears to be a general result for silicate glasses<sup>12</sup> and, indeed, for most amorphous solids. That is, the magnitude of the  $T^2$  thermal conductivity is roughly independent of chemical composition or thermal history. Nevertheless, the phonon mean free path is substantially smaller in the sol-gel than in vitreous silica.

An estimate of the phonon mean free path,  $l$ , at frequency  $\nu$  may be obtained from the equation

$$\kappa = 4\pi\nu^{-2}k(kT/h)^3 \int_0^{x_D} l(x)x^4 e^x (e^x - 1)^{-2} dx, \quad (3)$$

where  $x = h\nu/kT$ ,  $k$  and  $h$  are the Boltzmann and Planck constants, respectively, and  $x_D$  is the Debye temperature divided by  $T$ . The thermal conductivity of Fig. 1 may be accounted for with only two explicitly frequency-dependent contributions to  $l$ , namely

$$l^{-1} = A\nu^{1.2} + B\nu^n, \quad (4)$$

where  $l$  is in meters and  $\nu$  is in hertz. The first term in Eq. (4) approximates the phonon scattering by TLS and determines the magnitude and temperature dependence of the thermal conductivity for  $T \lesssim 1$  K. The parameter  $A$  is also slightly temperature dependent,<sup>2</sup> but this detail will be neglected for convenience. The second term in Eq. (4) causes the plateau to appear in  $\kappa$  at  $T \gtrsim 1$  K and will be discussed below. The resulting mean free paths have been plotted in Fig. 3, and the fit to the sol-gel data is shown in Fig. 4. The fitting parameters are listed in Table II. At frequencies less than  $10^{11}$  Hz, where TLS dominate the phonon scattering, the mean free path in the sol-gel is a factor of 3 smaller than that of vitreous silica.

From Eqs. (2) and (3) it may be noted that  $l \propto v^3 \rho / \gamma^2 \bar{P}$

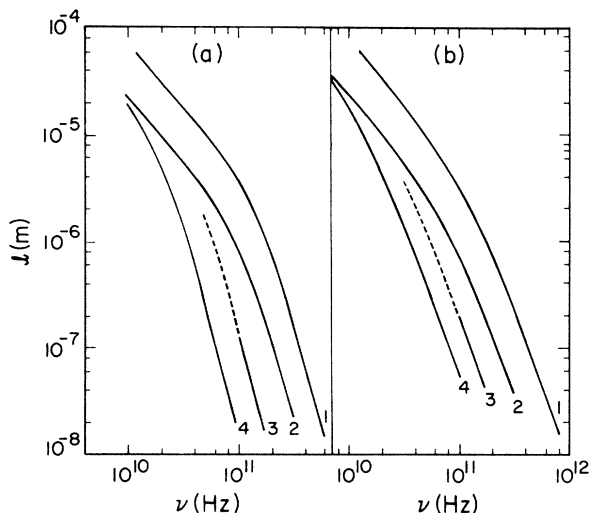


FIG. 3. Phonon mean free paths  $l$ , deduced from thermal-conductivity data, versus frequency  $\nu$  for silica glasses. Curves in (a) assume  $n=4$  in Eq. (4), while curves in (b) assume  $n=3$ . Curve 1 represents vitreous silica (Ref. 6), curve 2 is for sol-gel, curve 3 is for Vycor of nominal 40 Å pore diameter (Ref. 24), while curve 4 represents, for clarity, an average for two Vycor samples having pore diameters of 60 and 70 Å (Ref. 23). The dashed lines are extrapolations of the fits beyond the range of measurement. For all samples, the maximum frequency is less than  $\nu/d$ , see text.

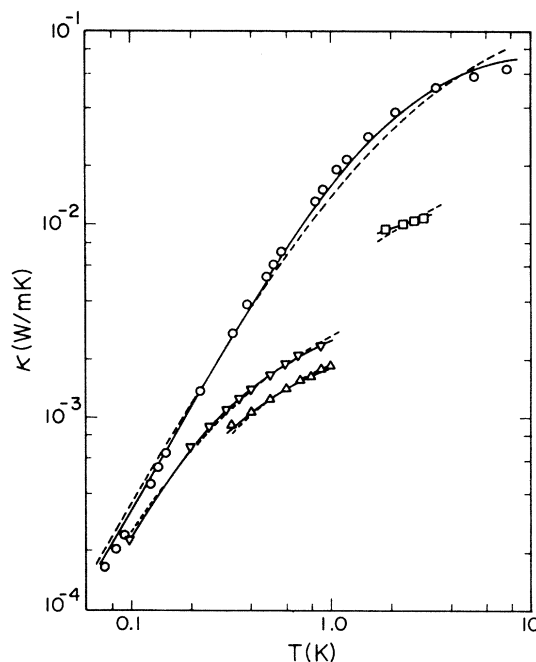


FIG. 4. Thermal conductivity of sol-gel glass ( $\circ$ ) and porous Vycor ( $\square$ , 40 Å;  $\nabla$ , 60 Å;  $\triangle$ , 70 Å). The solid lines are the computed conductivities using an inverse mean free path [Eq. (4)] containing the  $\nu^4$  term [Eq. (6)]; the dashed lines are computed using the  $\nu^3$  term [Eq. (5)].

TABLE II. Parameters obtained by fitting the two-term expression  $l^{-1} = Av^{1.2} + Bv^n$  to the thermal-conductivity data of silica glasses. The dimensions are m for  $l$ , Hz for  $v$ . For the Vycor samples, it is assumed that the porosity is  $r=0.28$  and that the phonon velocity is that given in Table I. The parameter  $d$  is the pore diameter computed from Eq. (5) or (6).

Sample	$n$	$10^8 A$	$B$	$d$ (Å)
Sol-gel	3	4.1	$8.4 \times 10^{-28}$	17–24
	4	4.5	$4.8 \times 10^{-39}$	21–26
Vycor	( $\approx 40$ Å pores) <sup>a</sup>	3	$4.8 \times 10^{-27}$	43
		4	$6.7 \times 10^{-38}$	53
	( $\approx 60$ Å pores) <sup>b</sup>	3	$1.6 \times 10^{-26}$	78
		4	$5.0 \times 10^{-37}$	103
	( $\approx 70$ Å) <sup>b</sup>	3	$2.4 \times 10^{-26}$	95
		4	$7.2 \times 10^{-37}$	116
Silica <sup>c</sup>	3	1.3	$1.3 \times 10^{-28}$	21–38
	4	1.4	$5.2 \times 10^{-40}$	26–38

<sup>a</sup>Reference 24.

<sup>b</sup>Reference 23.

<sup>c</sup>Reference 6.

for phonons scattered by TLS. This relation indicates that the ratio of  $\gamma^2 \bar{P}$  for the sol-gel relative to that of vitreous silica is 0.3. The value of 0.3 may be compared with the ratio of 15 for the TLS densities  $n$  obtained from the specific heat. Clearly, either a much smaller fraction of TLS interact strongly with phonons in the sol-gel, and/or the coupling constant  $\gamma$  is much smaller for the sol-gel.

The strength of the TLS-phonon coupling is often given in the form of a dimensionless parameter, namely  $C_0 = \bar{P}\gamma^2/\rho v^2$ . For the sol-gel,  $C_0$  is a factor of  $\approx 1.7$  greater than for vitreous silica; hence  $C_0$  for the sol-gel is  $\approx 5 \times 10^{-4}$ . This value is similar in magnitude to those values of  $C_0$ ,  $(3-10) \times 10^{-4}$ , found for silicate and fluoride glasses,<sup>13</sup> borate glasses,<sup>14</sup> amorphous polymers,<sup>15</sup> and even metallic glasses.<sup>16</sup> In this respect, the sol-gel is not a unique glass for temperatures  $\leq 1$  K.

In many glasses an empirical correlation has been found<sup>17</sup> between the phonon mean free path  $l$  and the glass transition temperature  $T_g$ . The value of  $l$  has conventionally been evaluated at 0.2 K where the thermal conductivity is well into the TLS regime, yet can be measured with accuracy. The magnitude is computed from  $l = 2.45 \times 10^{-11} \kappa v^2 T^{-3}$ . The empirical correlation is  $l_{0.2\text{ K}} \approx 4 \times 10^{-8} T_g$  (m) for oxide glasses.<sup>12,17,18</sup> It is of interest to investigate the validity of such a proportionality for our sol-gel. From Fig. 1,  $l_{0.2\text{ K}}$  was calculated to be  $1.5 \times 10^{-5}$  m. Therefore one would predict that the  $T_g$  for the sol-gel should fall near  $\approx 380$  K. This expectation is in agreement with predictions of dramatically reduced  $T_g$  in sol-gel glasses prior to final heat treatment.<sup>3</sup>

Differential thermal analysis of our sol-gel sample revealed a broad endothermic minimum near 400 K, as shown in Fig. 5. This minimum is no longer present upon

a second scan. Although the observed minimum is most definitely not a glass transition, it is indicative of the onset for mobility of organic residue and water in the glass structure,<sup>19,20</sup> and it does occur near where the empirical proportionality with  $l_{0.2\text{ K}}$  would predict a  $T_g$ . Hence, the sol-gel sample might be construed to have behavior similar to other oxide glasses with regard to the proportionality between mean free path and glass transition temperature.

As stated previously, the second term in Eq. (4) dictates the behavior of  $\kappa$  in the plateau at  $T \geq 1$  K in Fig. 1. For vitreous silica the physical origin of this term is not known.<sup>2,21</sup> However, for a porous silica glass, Vycor, the conductivity in the plateau regime is reduced in magni-

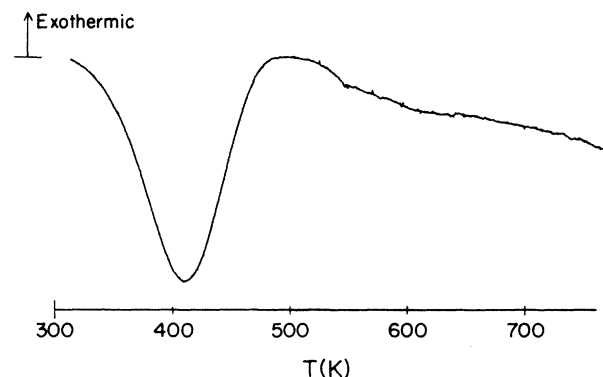


FIG. 5. Typical differential thermal analysis scan of the sol-gel product, showing an endothermic feature near 400 K.

tude by the scattering of phonons from the pores.<sup>22</sup> Thermal-conductivity data for porous Vycor<sup>23,24</sup> are included in Fig. 4. Since the sol-gel also contains pores, it is possible that the conductivity in the plateau is also limited by phonon-pore scattering. If the pores are roughly cylindrical in shape, then the second term of Eq. (4) is of the form<sup>22</sup>

$$Bv^3 = (13.6rd^2/v^3)v^3, \quad (5)$$

where  $r$  is the volume porosity and  $d$  is the pore diameter. On the other hand, if the pores are spherical then the second term of Eq. (4) would be of the form<sup>25</sup>

$$Bv^4 = (65rd^3/v^4)v^4. \quad (6)$$

These equations are valid provided  $d < v/v$ .

Values of  $B$  are listed in Table II for both fits, namely  $Bv^n$  with  $n=3$  or 4. The fitted curves are shown in Fig. 4. Knowing  $r$  and  $v$ , a pore diameter may be deduced using Eqs. (5) and (6). For the porosity of the sol-gel, a lower bound ( $r \approx 0.2$ ) is obtained by assuming the pores are voids. An upper bound ( $r \approx 0.3$ ) is obtained under the assumption that the bulk material of sol-gel is vitreous silica while the pores are filled with H<sub>2</sub>O. In this case, the scattering terms of Eqs. (5) and (6) are multiplied by the factor  $(\delta\rho/\rho)^2$ , where  $\delta\rho$  is the difference in mass density between H<sub>2</sub>O and silica.

The deduced pore diameters are given in the last column of Table II, the range of values for sol-gel representing the uncertainty in  $r$ . The result for sol-gel, namely  $d \approx 20$ – $30$  Å, agrees with pore sizes deduced from other studies.<sup>4,5</sup> Also, for the Vycor, our deduced values of  $d$  agree within a factor of 2 with values quoted by the respective authors. The apparent discrepancies between calculated and nominal values of pore diameter for the Vycor could easily be accounted for by the lack of precise knowledge of phonon velocities and porosities. In brief, the thermal conductivities of sol-gel and Vycor at  $T \approx 1$ – $10$  K can be accounted for by the "classical" scattering of thermal phonons by pores.

As is evident from Fig. 3, vitreous silica also exhibits a drop-off in phonon mean free path<sup>26</sup> (plateau in thermal conductivity). However, if this feature was attributable to scattering from pores, the pore diameters<sup>27</sup> would have to be 20–40 Å. These pore diameters are an order of magnitude larger than the expected pore sizes in vitreous silica.<sup>28</sup>

An alternative explanation for the plateau for sol-gel and Vycor derives from the possible fractal nature of the material.<sup>10,29</sup> In this case, the phonon mean free path is expected to become increasingly smaller with increasing  $v$

until the nature of the excitation spectrum crosses over from phonons to localized fractons. In the fracton model, the phonon mean free path  $l$  is expected to vary as  $v^{-4}$  at frequencies below the crossover, and the parameter  $B$  of Eq. (4) is related to the correlation length of the fractal network.<sup>30</sup> We have already noted that  $l \propto v^{-4}$  provides a satisfactory explanation for the data of Fig. 4. Hence, for phonons having  $v \lesssim 3 \times 10^{11}$  Hz, scattering by pores and scattering due to the fractal nature of the solid may be considered to be equivalent viewpoints. Alternatively, it may be stated that the data of Fig. 4 are not an unmistakable manifestation of a non-Euclidean structure of sol-gel or porous Vycor. A similar comment may be applied to the reduction in ultrasonic velocity with porosity.

It has been speculated<sup>10</sup> that amorphous materials in general are fractal, and that the plateau in the thermal conductivity is caused by the crossover from phonons to localized fractons. The predicted  $l \propto v^{-4}$  is consistent with measurements on vitreous silica. However, the magnitude of  $l$  has not been computed from the fracton theory and so a quantitative test is not possible.

In summary, measurements on an uncompacted sol-gel sample are indicative of a density of TLS that is 15 times greater than for vitreous silica, sound velocities that are roughly one-half those of vitreous silica, and a thermal conductivity in the  $\kappa \propto T^2$  (TLS) regime that is roughly the same as that of vitreous silica. In the TLS regime at  $T \lesssim 1$  K, the phonon mean free path is reduced by a factor of 3 relative to vitreous silica. The empirical relation  $l_{0.2\text{K}} \propto T_g$  observed for other oxide glasses predicts a reduction of  $T_g$  for the sol-gel relative to that of vitreous silica. Differential thermal analysis of the sol-gel reveals the onset of mobility and evolution of residual ethanol and water near the predicted  $T_g$ . At temperatures  $> 1$  K, the thermal conductivity in the plateau appears to be dominated by the scattering of phonons by pores intrinsic to the sol-gel, which is similar to the behavior found in porous Vycor. The sol-gel data do not provide conclusive evidence of fractal behavior.

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