

## Low-Temperature Specific Heat and Thermal Conductivity of Silica Aerogels

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Specific-heat and thermal-conductivity measurements were made on a series of base-catalyzed silica aerogels at temperatures between 0.05 and 20 K. Evidence for a crossover between regimes of characteristically different excitations was observed. The data analysis indicates a “bump” in the density of vibrational states  $g(\omega)$  at the crossover frequency from phonon to fracton behavior.

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Usually the lattice specific heat of crystalline matter is fairly well described by the Debye model, in principle a continuum approximation, if  $T \ll \Theta_D$ , where  $k_B \Theta_D$  is the cutoff energy. Although *a priori* not obvious, it became clear that this continuum model is not sufficient to describe the low-temperature specific heat of disordered solids, where additional degrees of freedom need to be considered. Well known in this respect are the two-level states of amorphous materials.<sup>1</sup> More recently, descriptions of the behavior of certain disordered solids introduced the fractal concept. Typical representatives of this kind of substance are aerogels, i.e., silica oxides with very low densities of typically only 5%–10% of conventional glasses. Small-angle x-ray<sup>2</sup> and neutron scattering<sup>3</sup> identify three structural regions. At the largest length scales the material appears homogeneous and at the smallest length scales one observes the individual building blocks consisting of dense amorphous SiO<sub>2</sub> particles. In between, one finds power-law behavior in the density correlation function, giving a Hausdorff dimension in the range from 1.9 to 2.4.<sup>3</sup> In terms of the dynamics of these systems again three regions of distinctly different behavior, characterized by the frequency dependences of the excitation densities of states (DOS)  $g(\omega)$ , have been proposed. At very low frequencies, a normal Debye-type behavior is expected [ $g(\omega) \propto \omega^2$ ]. In between two crossover frequencies, the fractal region is characterized by local fracton states with  $g(\omega) \propto \omega^{\bar{d}-1}$ , where  $\bar{d}$  is termed the spectral dimension.<sup>4</sup> At high frequencies, the dynamics of the small amorphous particles dominates.

There is much controversy about the frequency dependence of the DOS at the phonon-fracton crossover in fractal structures. Based on scaling arguments,<sup>5</sup> it is claimed that a peak should be observed at the crossover frequency  $\omega_{co}$ , and effective-medium-approximation calculations<sup>6</sup> indicate a rapid variation of  $g(\omega)$  at  $\omega_{co}$ . Light-scattering experiments on *neutrally reacted* aerogels,<sup>7</sup> and inelastic neutron-scattering experiments on *base-catalyzed* samples,<sup>8</sup> however, have been interpreted to indicate the absence of anomalies in the DOS. Simulations carried out on two-dimensional networks of random springs also show no bump in the DOS at the

phonon-fracton crossover.<sup>9</sup> Spin-echo neutron data, however, indicate a peak in the density of states for base-catalyzed samples,<sup>10</sup> while no such anomaly is deduced from the data of neutrally reacted specimens.<sup>10,11</sup> The difference in behavior has been ascribed to distinct differences in the structural texture between neutrally reacted and base-catalyzed aerogels.

In an attempt to strengthen the experimental basis for theoretical concepts addressing the above-mentioned issues, we have measured  $C_P$  and the thermal conductivity  $\lambda$  down to temperatures of 0.05 K in three homologous *base-catalyzed* aerogel samples<sup>12</sup> because, as given by Eq. (1),  $C_P(T)$  only depends on  $g(\omega)$ , and the energy range of the excitations in question can be mapped with a single type of experiment. Previous work involving this type of measurement<sup>13</sup> covered the range from high-temperature behavior well into the fracton region but, to our knowledge, the present  $C_P(T)$  results are the first that allow a discussion of the lower crossover mentioned above. They indicate that indeed there is a peak in the density of states in the neighborhood of the phonon-fracton crossover frequency of *base-catalyzed* aerogels.

All our samples<sup>12</sup> were prepared using the same recipe, but with differing densities of  $\rho = 0.145, 0.190,$  and  $0.275 \text{ g/cm}^3$ . Treatments that affect the internal surface, like oxidation, modify the values of  $C_P$  at high temperatures but do not affect the value of  $C_P$  below 2.5 K.<sup>14</sup> Compared to amorphous silica,  $\lambda(T)$  can be up to 3 orders of magnitude smaller for temperatures in the range from 0.1 to 20 K, while, in contrast,  $C_P(T)$  may be more than an order of magnitude larger. Large  $C_P$  and small  $\lambda$  make conventional methods for the measurement of these thermal properties difficult. Hence, we have developed a dynamic technique for measuring simultaneously  $C_P$  and  $\lambda$  of poor thermal conductors, which can be considered as an extension of a relaxation method. It involves the analysis of the nontrivial temperature relaxation of the sample after cutting the heating power and is described in detail elsewhere.<sup>15</sup> Various test experiments comparing samples with distinctly different geometries confirmed that the method gives reliable results also at very low temperatures.

Our samples were characterized with small-angle neu-

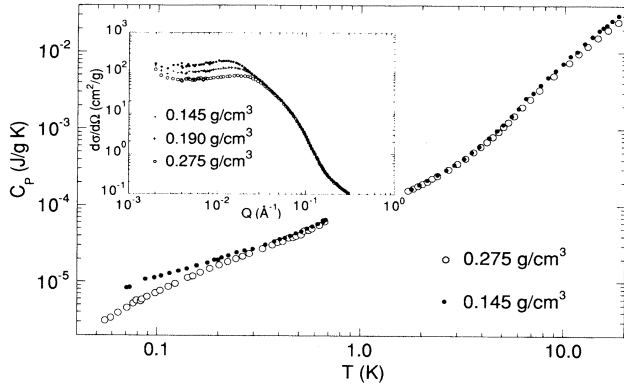


FIG. 1. Plot of  $\log C_P$  vs  $\log T$  for two aerogel samples with  $\rho=0.145$  and  $0.275 \text{ g/cm}^3$ , respectively, at low temperature. Inset: The results of the small-angle neutron-scattering experiments on materials with three different densities.

neutron scattering (SANS) and the results are shown in the inset of Fig. 1. The scattering data can be scaled with characteristic lengths  $\xi$  depending on the density with a fractal dimension of  $\sim 2$ .<sup>16</sup> The size of the basic particles is  $R=20 \text{ \AA}$  for all specimens. The results of a direct measurement of both the longitudinal ( $v_L$ ) and transverse ( $v_T$ ) speed of sound using a pulse-echo method<sup>17</sup> are listed in Table I.

In Fig. 1 our  $C_P$  data for two aerogels with densities  $0.145$  and  $0.275 \text{ g/cm}^3$  are shown for all temperatures measured. Above  $0.6 \text{ K}$ ,  $C_P$  is about the same for the two materials and is approximately linear in  $T$  in the range between  $0.6$  and  $2.5 \text{ K}$ . An enhanced temperature dependence of  $C_P$  is noted at higher temperatures. Our low-temperature data, which we do not expect to be influenced by the internal vibrational modes of the individual particles ( $20 \text{ \AA}$ ), are plotted in Fig. 2 as  $C_P/T$  vs  $T$ . At low temperatures ( $T < 0.3 \text{ K}$ ) the specific heat for the material with highest density ( $\rho=0.275 \text{ g/cm}^3$ ) clearly decreases faster with  $T$  than for the low-density ( $\rho=0.145 \text{ g/cm}^3$ ) material. For the latter material the  $C_P/T$  ratio increases with decreasing  $T$  down to the lowest temperature measured ( $0.065 \text{ K}$ ). In contrast, for the high-density sample there is a distinct drop in  $C_P/T$  at about  $0.12 \text{ K}$ . Both trends indicate, as we argue below, the crossover between the fracton and phonon regimes. Because  $C_P$  depends only on the density of states  $g(\omega)$  as

$$C_P = \frac{k_B^2 T}{\hbar} \int_0^\infty g \left( \frac{k_B T}{\hbar} x \right) \frac{x^2 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where  $x = \hbar \omega / k_B T$ , one can obtain information about the DOS from fits to  $C_P(T)$ . In a first attempt we used  $g(\omega)$  as has been suggested by Schaefer *et al.*<sup>10</sup> and implicitly by Courtens *et al.*,<sup>7</sup> assuming a smooth phonon-

TABLE I. Measured velocities of sound and parameters obtained from fits of Eq. (3) to data (see text). The average relative uncertainty of these parameters is estimated to be 2%.

Density ( $\text{g/cm}^3$ )	Pulse-echo results			$T_{co}$ (K)	$C_P$ results	
	$v_L$ (m/s)	$v_T$ (m/s)	$v_s$ (m/s)		$\bar{d}$	$g_{fr}(k_B T_{co}/\hbar)$ (s/g)
0.145	182	107	119	0.10	1.11	$1.11 \times 10^7$
0.190	252	158	174	0.18	1.07	$1.32 \times 10^7$
0.275	423	265	292	0.37	1.21	$9.88 \times 10^6$

fracton crossover in the DOS that is given by

$$g(\omega) \propto \frac{\omega^2}{(\omega_{co}^2 + \omega^2)^{(3-\bar{d})/2}}, \quad (2)$$

which has no bump if  $\bar{d} > 1$ . This DOS was claimed to be consistent with results of Brillouin light-scattering measurements<sup>18</sup> of *neutrally reacted* aerogels and neutron spin-echo data<sup>10,11</sup> of *neutrally reacted* samples, as well as a *base-catalyzed* sample. The results of the neutron spin-echo measurements on the *base-catalyzed* sample, however, were qualitatively different from those of the *neutrally reacted* samples, yielding a large DOS at small energies, decaying toward zero at higher energies. Because of unsatisfactory fits, we have considered a second possibility, allowing for an abrupt crossover by assuming

$$g(\omega) \propto \begin{cases} \omega^2 & \text{for } \omega < \omega_{co}, \\ \omega^{\bar{d}-1} & \text{for } \omega > \omega_{co}. \end{cases} \quad (3)$$

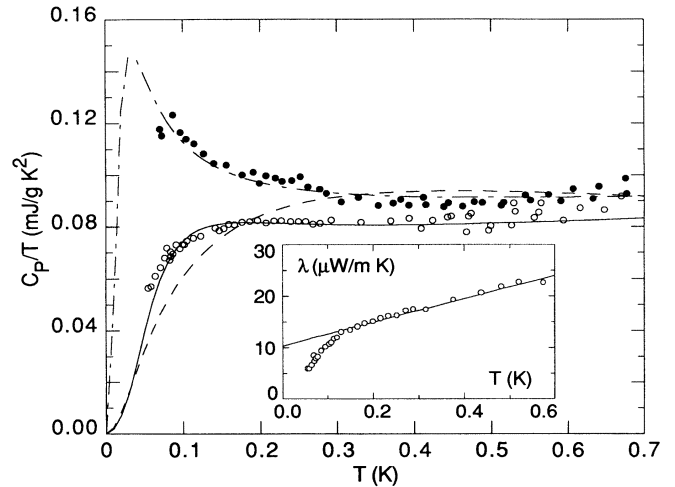


FIG. 2.  $C_P/T$  vs  $T$  between  $0.05$  and  $0.6 \text{ K}$  for high-density (open circles) and low-density (solid circles) samples. For the high-density sample the solid line is the best fit using Eq. (3), and the dashed line is the best fit using Eq. (2). The dash-dotted line is the best fit with Eq. (3) for the low-density sample. Constraints of the fits are described in the text. Inset:  $\lambda(T)$  between  $0.05$  and  $0.6 \text{ K}$ . The solid line is a fit as described in the text.

This is similar to the model discussed by Conrad *et al.*,<sup>8</sup> except that in our case no attempt is made to assure continuity of  $g(\omega)$  at  $\omega = \omega_{co}$ . From the low-frequency velocity of sound  $1/v_s^3 \equiv (1/v_L^3 + 2/v_T^3)/3$ , the low-temperature ( $T \ll T_{co} \equiv \hbar \omega_{co}/k_B$ ) specific heat can be computed<sup>19</sup> by  $C_P = (2\pi^2/5)k_B^4 T^3 / (\hbar v_s)^3 \rho$ . We fitted either model to the data with the constraint that the low-temperature specific heat be given by this calculation. We find that the model of Eq. (3) provides by far the best fit, and when extracting the DOS from the fit parameters we obtain a large discontinuity in the DOS resulting in a sharp peak near  $T_{co}$  (Fig. 3). The resulting fit parameters,  $T_{co}$ ,  $\bar{d}$ , and  $g_{fr}(\omega_{co})$  (density of fracton states), for all three densities are given in Table I. A fit based on  $g(\omega)$  given in Eq. (2) yields a significantly larger  $\chi^2$  than that for Eq. (3) and it may be seen in Fig. 2 that the features of the data for the high-density sample are poorly reproduced. Calculating  $C_P(T)$  by using Eq. (2) and the parameters for an aerogel that corresponds to our 0.19-g/cm<sup>3</sup> sample given in Ref. 10 results in a curve that is far from the observed behavior.

Information on the DOS with respect to the  $T$  axis as obtained by  $C_P(T)$  results is complementary to information obtained directly on the  $\omega$  axis by means of scattering experiments. Considering Eq. (1),  $C_P(T)$  is relatively insensitive to the exact details of the DOS. In addition, rounding effects due to the lifetime broadening of the modes is expected. The interpretation of scattering experiments, however, requires knowledge of sample-dependent amplitude factors. Thus,  $g(\omega)$  as shown in Fig. 3 should be interpreted as giving the trend that we derive from our experiments. The essential difference between the two empirical fits is the presence of an anomaly using Eq. (3), which does not appear in Eq. (2).

Allowing all parameters to vary freely without constraining the low-temperature  $C_P$  to be given from the measured velocity of sound, Eq. (3) again leads to the

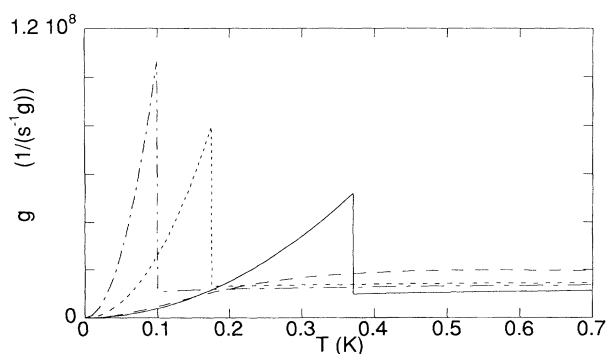


FIG. 3. Density of states  $g(\omega)$  resulting from the best fits using Eq. (2) or (3). Long-dashed line,  $\rho = 0.275$  g/cm<sup>3</sup>, Eq. (2); solid line,  $\rho = 0.275$  g/cm<sup>3</sup>, Eq. (3); short-dashed line,  $\rho = 0.19$  g/cm<sup>3</sup>, Eq. (3); and dash-dotted line,  $\rho = 0.145$  g/cm<sup>3</sup>, Eq. (3).

best agreement with experiment and a fit value for the highest-density sample of  $v_s = 265$  m/s, in reasonable agreement with the independently measured (by pulse-echo technique) value of  $v_s = 292$  m/s. For the other two samples the covered temperature range into the crossover regime is small and therefore no information can be obtained about the velocity of sound for them. We also note that from our fits the amplitude of the  $g(\omega)$  mismatch at  $\omega_{co}$  increases with decreasing sample density. The  $\rho$  dependences of both the independently measured  $v_s$  and the fitting values of  $\omega_{co}$  imply that  $g(\omega_{co}^-)$  should increase with decreasing  $\rho$  in the phonon approximation while, assuming mutual self-similarity,  $g(\omega_{co}^+)$  should remain approximately constant where the fracton approximation of our model applies. The trends of  $g(\omega_{co})$  in Fig. 3 are consistent with this expectation.

An example of our data for the thermal conductivity  $\lambda$  is shown in the inset of Fig. 2. We observe for the high-density sample, at about 0.13 K, a sharp drop in  $\lambda$  as  $T$  is decreasing. No such drop is observed in the low-density sample down to the lowest temperature measured of 0.1 K. We find that at temperatures above this dropoff, the thermal conductivity of the high-density sample closely obeys  $\lambda = A + BT$ , with  $A = 1.04 \times 10^{-5}$  W/m K,  $B = 2.3 \times 10^{-5}$  W/m K<sup>2</sup> up to about 4 K. This linear behavior, which is demonstrated by the straight line in the inset of Fig. 2 for data below 0.6 K, holds over a factor of 30 in temperature. We interpret the reduction in the slope of  $\lambda(T)$  with increasing temperature from below to above 0.13 K in the high-density sample to be due to the saturation of the low-frequency phonon modes, while the higher-frequency fracton modes are localized, and therefore cannot carry heat. The fact that  $\lambda$  is not constant for temperatures above the crossover temperature (i.e.,  $B \neq 0$ ) has been discussed in reference to other disordered materials showing this  $\lambda(T)$  behavior.<sup>20</sup> A theory based on nonlinear coupling between fractons and phonons has been proposed to explain this observation.<sup>21</sup> A more extensive presentation and discussion of our thermal-conductivity data will be presented elsewhere.<sup>22</sup>

The approximately linear  $T$  behavior of  $C_P$  above the crossover temperature might be suggestive of the presence of the "two-level systems" used to explain the linear  $T$  dependence of  $C_P$  and the concomitant  $T^2$  variation of  $\lambda$  in glasses.<sup>1</sup> This coincidence usually found for glassy materials is, however, *not* observed in our case and therefore it is reasonable to postulate a characteristically different physical cause for the behavior of aerogels. Unfortunately, measurements of  $C_P$  only give information about the frequency dependence of the DOS and cannot in principle determine its physical origin. However, if the almost linear behavior in  $C_P$  were simply due to two-level systems, we would not expect to see a distinct decrease of  $C_P/T$  (and of  $\lambda$ ) at low temperatures as we observe (Fig. 2).

In conclusion, we have measured the low-temperature specific heat and thermal conductivity of a series of

*base-catalyzed* silica aerogels which, by scattering experiments, were found to exhibit the same structural characteristics as generally found for aerogels. Assuming the existence of both phonon and fracton modes, we find evidence for the crossover between these modes. We deduce that an anomaly in the density of excitation modes at frequencies in the vicinity of the crossover frequency is essential to explain our  $C_p(T)$  results, in line with claims of published theoretical work.<sup>5</sup> In view of the present situation, similar measurements on *neutrally reacted* aerogels seem highly desirable.

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<sup>1</sup>P. W. Anderson, B. I. Halperin, and C. M. Varma, *Philos. Mag.* **25**, 1 (1972).

<sup>2</sup>D. W. Schaefer and K. D. Keefer, *Phys. Rev. Lett.* **56**, 2199 (1986).

<sup>3</sup>R. Vacher, T. Voignier, J. Pelous, and E. Courtens, *Phys. Rev. B* **37**, 6500 (1988).

<sup>4</sup>S. Alexander and R. Orbach, *J. Phys. (Paris), Lett.* **43**, L625 (1982).

<sup>5</sup>A. Aharony, S. Alexander, O. Entin-Wohlman, and R. Orbach, *Phys. Rev. B* **31**, 2565 (1985); P. F. Tua and S. J. Putterman, *Phys. Rev. B* **33**, 2855 (1986).

<sup>6</sup>B. Derrida, R. Orbach, and Kin-Wah Yu, *Phys. Rev. B* **29**, 6645 (1984).

<sup>7</sup>E. Courtens, R. Vacher, J. Pelous, and T. Voignier, *Euro-*

*phys. Lett.* **6**, 245 (1988).

<sup>8</sup>H. Conrad, U. Buchenau, R. Schätzler, G. Reichenauer, and J. Fricke, *Phys. Rev. B* **41**, 2573 (1990).

<sup>9</sup>K. Yakubo and T. Nakayama, *Phys. Rev. B* **36**, 8933 (1987); K. Yakubo, E. Courtens, and T. Nakayama (to be published).

<sup>10</sup>D. W. Schäfer, C. J. Brinker, D. Richter, B. Farago, and J. Frick, *Phys. Rev. Lett.* **64**, 2316 (1990).

<sup>11</sup>E. Courtens, C. Lartigue, F. Mezei, R. Vacher, G. Coddens, M. Foret, J. Pelous, and T. Woignier, *Z. Phys. B* **79**, 1 (1990).

<sup>12</sup>Obtained from AB Airglass, Staffanstorp, Sweden.

<sup>13</sup>A. M. De Goer, R. Calemczuk, B. Salce, J. Bon, E. Bonjour, and R. Maynard, *Phys. Rev. B* **40**, 8327 (1989).

<sup>14</sup>A. Bernasconi, T. Sleator, D. Posselt, and H. R. Ott, in *Proceedings of the International Conference on Low-Temperature Physics*, LT 19, Brighton, 1990 [*Physica (Amsterdam) B* (to be published)].

<sup>15</sup>A. Bernasconi, T. Sleator, D. Posselt, and H. R. Ott, *Rev. Sci. Instrum.* **61**, 2420 (1990).

<sup>16</sup>D. Posselt, thesis, Risø National Laboratory, Denmark, 1990 (unpublished).

<sup>17</sup>J. Gross, G. Reichenauer, and J. Fricke, *J. Phys. D* **21**, 1447 (1988).

<sup>18</sup>R. Vacher, E. Courtens, G. Coddens, A. Heidemann, Y. Tsujimi, J. Pelous, and M. Foret, *Phys. Rev. Lett.* **65**, 1008 (1990).

<sup>19</sup>N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt-Saunders, Tokyo, 1981).

<sup>20</sup>J. E. de Oliveira, J. N. Page, and H. M. Rosenberg, *Phys. Rev. Lett.* **62**, 780 (1989).

<sup>21</sup>S. Alexander, O. Entin-Wohlman, and R. Orbach, *Phys. Rev. B* **34**, 2726 (1986).

<sup>22</sup>D. Posselt, J. K. Kjems, A. Bernasconi, T. Sleator, and H. R. Ott (to be published).