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Bourret

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LOW ENERGY EXCITATIONS IN SILICA AEROGELS

R. MAYNARD, R. CALEMCZUK*, A.M. DE GOER*, B. SALCE*, J. BON*,
E. BONJOUR* and A. BOURRET**

CNRS, CRTBT, BP 166X, F-38042 Grenoble Cedex, France

*CENG, DRF/SBT-LCP, BP 85X, F-38041 Grenoble Cedex, France

**CENG, DRF/SPh-S, BP 85X, F-38041 Grenoble Cedex, France

Résumé - La chaleur spécifique, la conductivité thermique, le frottement interne et les variations relatives de la vitesse du son ont été mesurés entre 0.1 K et 10 K sur des aérogels de silice de faible densité ($\rho < 0.8 \text{ g/cm}^3$). En s'appuyant sur des observations de microscopie électronique, les résultats ont été analysés dans un modèle où l'on a calculé les propriétés élastiques d'un ensemble hiérarchique désordonné de tiges.

Abstract - Specific heat, thermal conductivity, internal friction and relative change in sound velocity measurements have been performed from 0.1 K to 10 K on several low density silica aerogels ($\rho < 0.8 \text{ g/cm}^3$). Taking into account electron microscope observations, the results have been analysed within a model where the elastic properties of a hierarchical disordered network of rods are calculated.

1 - INTRODUCTION

Solids exhibiting a dilation-symmetry can be described by using a non-integer mass scaling exponent, the "fractal" dimension $\bar{d}$ lower than the embedding Euclidean space dimension d . In this case, the density for large samples vanishes like $\rho \sim r^{d-\bar{d}}$. This property has led to consider the highly inhomogeneous low density silica aerogels as valuable candidates to exhibit such fractal structures /1,2/. On the other hand, it has been expected that, from a dynamical point of view, the behavior of these structures should be markedly different from homogeneous dense solids and that new type of excitations (for example, the so-called "fractons") exist in these compounds /3/. In this paper, we present a set of experimental results on low temperature thermal properties carried out on light ($\rho < 0.9 \text{ g/cm}^3$) silica aerogels in the temperature range 0.1 K $\rightarrow$ 10 K. Grounded on high resolution microscope observations /4/, these results have been interpreted in the framework of the elastic properties of a hierarchical network of rods, in order to try to understand what the microscopic origins of the low energy excitations are /5/.

2 - SAMPLES AND EXPERIMENTS

The low density silica aerogels were prepared by hydrolysis of tetrametoxysilane in methanol and by removing the solvent in hypercritical conditions. Gels of higher density ($\rho > 0.4 \text{ g/cm}^3$) were annealed at 700° C under H_2 atmosphere (densified aerogels). The neutral reacted aerogels (N) were supplied by "Laboratoire des Sciences des Matériaux Vitreux", Montpellier (France) and belong to a set of samples also studied by Brillouin /1/ and Raman /6/ scattering. The base catalysed gels (B) came from C.E.N. Saclay (France). High resolution electron microscope observations have shown that both basic and neutral aerogels exhibit open structures of small rods interconnected at random, but differences lie in the size of the rods (Table 1). Room temperature sound velocities scaled with the density: $V \sim \rho^b$, with $b = 1.25$ for the basic gels /7/ and $b = 1.55$ for the neutral serie /1/. Thermal and acoustic measurements performed on aerogels present specific difficulties mainly connected with their very poor thermal diffusivity and the brittleness of the less dense samples. Moreover, the high porosity of the specimens compel us to pay attention to avoid the presence of residual gases (e.g. : helium) inside the samples.

Table 1

Experimental results obtained on silica aerogels. a_0 , a_1 and a_2 are the branch diameters of the different hierarchical stages /4/ (see : 4 - ANALYSIS).

Sample	$\rho(\text{g/cm}^3)$	$V_L(\text{cm/s})$ $\times 10^5$	$a_0(\text{\AA})$	$a_1(\text{\AA})$	$a_2(\text{\AA})$	δ
B - (a) : o	0.87	1.85	-	-	-	1.64
B - (c) : •	0.27	0.425	50 ± 10	-	-	1.15
N - (1) : +	0.36	0.78	2.8	31 ± 7	-	1.45
N - (3) : Δ	0.12	-	2.8	30 ± 17	250 ± 110	1.37

The specific heat $C_p(T)$ measurements have been performed using an adiabatic method. Particular care was taken to remove the adsorbed molecules at room temperature and several experiments were performed in order to estimate their contribution to $C_p(T)$. The final accuracy on $C_p(T)$ is about 5 %. The results below 10 K are reported in figure 1.1, together with a curve representative of the classical dense disordered solid $\alpha\text{-SiO}_2$, in a $C_p(T)/T^3$ versus T plot which clearly shows the strong difference with the T^3 behavior expected for an homogeneous solid. In figure 1.2 are plotted the results for gels (a) and (c) up to 100 K. Thermal conductivity $K(T)$ measurements were made using the classical steady state method, inside a vacuum jacket ($p \sim 10^{-6}$ torr) evacuated at room temperature. The accuracy was estimated to be ~ 10 %. Due to the very poor conductivity of aerogels, measurements above 10 K have not been performed yet. The results for samples (a), (c) and (1) are displayed in figure 2.

Fig. 1 - Specific heat of SiO_2 aerogels. o : B-(a) ; • : B-(c) ; + : N-(1) ; Δ : N-(3). Solid line : Bulk $\alpha\text{-SiO}_2$. Broken line : Crystalline quartz. Left: fig.1.1 ; Right: fig.1.2

Fig. 2 - Thermal conductivity of SiO_2 aerogels. o : B-(a) ; • : B-(c) ; + : N-(1). Solid line : Bulk a- SiO_2 .

3 - QUALITATIVE DISCUSSION

From the low temperature thermal behavior of aerogels, two different temperature ranges can be distinguished :

Below 2 K, the specific heat per unit of mass is very high (more than 50 times larger than that of bulk silica at 0.5 K), nearly density independent as long as $\rho < 0.3 \text{ g/cm}^3$ and exhibit a temperature variation which follows a power law of temperature $C_p(T) \sim T^8$. The values of δ deduced from the data are given in Table 1. However, it has been established that the measured $C_p(T)$ values are always lower than the corresponding Debye contributions calculated from the measured sound velocities /2/. This behavior differs markedly from what is observed for a- SiO_2 : $C_p(T)$ displays an excess regarding to the Debye contribution, which is assigned to anharmonic excitations (Two Level Systems). From the results of acoustical measurements carried out on gels (a), (c) and (1) /8/, it is deduced that the number of TLS per unit of mass in aerogels is of the same order of magnitude than in a- SiO_2 . Then, their contribution to $C_p(T)$ can be neglected. In the same temperature range, $K(T)$ exhibits a plateau-like feature. This behavior is strongly unusual since, in glasses, the plateau lies above 2 K. Concerning a more detailed comparison with the compact material a- SiO_2 , the plateau in gels is not accompanied by an excess in specific heat. This plateau can be qualitatively accounted for by assuming that low energy propagating phonons become localized above a cross-over temperature T_c , ranging from .06 K to .4 K.

Above 2 K, $C_p(T)$ approaches the specific heat of bulk silica but remains a bit larger up to 100 K. For the 3 measured samples, $K(T)$ roughly increases in the same monotonic way $T^{1.3 \pm .1}$, larger than the variation expected from the fracton theory /9/. As a final remark, we want to underline that $K(T)$ for the densified aerogel (a) looks very similar to those of light aerogels, in contrast with the specific heat results which seem to distinguish between the two types of materials, as the coefficients δ are markedly different.

4 - ANALYSIS

The simplest theory is based on the dilation invariance of the fractal structure in a range of length scale smaller than ξ . Beyond this length scale, the material is supposed to be homogeneous. The invariance is reflected in the dynamical properties by using a single scaling parameter of the macroscopic properties, the spectral (or fracton) dimension $\tilde{d}$. The fracton theory is phenomenological in the sense that $\tilde{d}$ is extracted from the experiments but cannot be calculated a priori. Our purpose is to try to interpret our results by calculating the fracton parameter $\tilde{d}$. The starting point for this microscopic description is to use a simple modelization of the observed structure of aerogels as a hierarchical network of rods, and to calculate the mechanical properties of such a structure (figure 3) /10/.

Fig. 3 - Structure of aerogels. Left : Sketch drawn from high resolution electronic microscope stereoview observations (Basic gel). Right : Theoretical modelization

Let us call n the different stages of the hierarchy and n^* the upper level : $n = 0, 1, \dots, n^*$. At the level n , the network can be considered as a disordered lattice made up with rods of length ℓ_n and thickness a_n . The aspect ratio $\lambda = \ell_n / a_n$ is independent of n since it is assumed a self-similar structure of the network. Besides, the network is described by a half-coordination number $\chi = Z/2$ where Z is the number of the next nearest neighbours. From one stage to the next one, lengths are expanded by an inflation ration h defined by $\ell_n = h \cdot \ell_{n-1}$ and $a_n = h \cdot a_{n-1}$ (in figure 3, the hierarchical structure is schematically pictured as a regular square lattice with $\chi = 4/2$). From the relation between the number of rods of stage n as a function of the same number at stage $n-1$: $N_{n-1} = h^3 \times \lambda^{-2} N_n$, one establishes that :

$$\rho_n = (1/\theta_1^n) \rho_0 \quad \theta_1 = \lambda^2 / \chi$$

ρ_0 is the mass density of the constitutive material ($\theta_1 > 1$). Now, in a "coarse-grained" sense, a fractal dimension $\tilde{d}$ can be defined as the ratio of the relative decrease of ρ over the relative increase of length scale :

$$\tilde{d} = \frac{\log(h^3/\theta_1)}{\log h} \quad (1 < \chi < \lambda^2 < h^2)$$

Assuming that the flexion of the constitutive rods of the network is the basic phenomena for the elastic properties, the macroscopic elastic constant E_n is directly related to E_{n-1} by :

$$E_n = (C\eta\lambda^{-4}) E_{n-1} = (\theta_2^{-1}) E_{n-1}$$

C describes the degree of constraints at the ends of the rods and η the fraction of the bent rods of the disordered network under a compressional stress. With the assumption of the elastic self-similarity, one gets :

$$E_n = (\theta_2^{-n}) E_0 = (\rho_n / \rho_0)^a E_0 \quad \text{with : } a = \frac{\log \theta_2}{\log \theta_1}$$

The value of the exponent a depends on 3 geometrical and 1 elastic parameters and can be fitted to the experiment. For neutral silica aerogels, $a \simeq 4$. From the structural determination of the geometrical parameters : $\lambda = 2.3$, $h = 12.4$ /4/ and $\bar{d} = 2.4$ /1/, one gets : $\chi = 1.17$ and $\theta_1 = 4.54$. From the scaling law of the sound velocities, $V \sim \rho^b$ with $b \simeq 1.5$, we obtain $C\eta = 0.056$. Then, the exponents a and b are dependent on the geometrical and elastic parameters of the model and there is no large universal property like in the problem of percolation.

Concerning the vibrations in the hierarchical network, a vibration of wavelength in the range (ℓ_n, ℓ_{n+1}) will experience the elastic constant of the material at this stage n . Two types of modes are considered :

- Compressional (or shearing) modes with a linear dispersion relation :

$$\omega_n \sim V_{n-1} k \sim \ell_n^{-1} V_{n-1}$$

- Flexural modes with a quadratic dispersion relation :

$$\omega_n \sim a_n V_{n-1} k^2 \sim \ell_n^{-1} V_{n-1}$$

Hence, both categories of modes give the same dependence on n for ω_n . From the previous elasticity relations, we obtain : $\omega_n = (\theta_3 h)^{-n} \omega_0$ for all the modes. Due to the disorder, an average curve along the frequency thresholds can be defined as :

$$\omega \sim k^\alpha \quad \text{with} \quad \alpha = \log(\theta_3 h) / \log h \quad (\alpha > 1)$$

In this case, one can define the spectral dimension $\tilde{d}$ for the spectral density by the relation : $g(\omega) \sim \omega^{\tilde{d}-1}$.

It is possible to calculate the exponent by determining the number of modes at each stages of the hierarchy :

$$\nu_n = N_n / N_0 = (\theta_1 h^{-3})^n$$

The average slope of $\log \nu(\omega)$ as a function of $\log \omega$ is called spectral or "fracton" dimension $\tilde{d}$. Its value is given by the relation :

$$\tilde{d} = \frac{\log (h^3 / \theta_1)}{\log (h \theta_3)} = \frac{\tilde{d}}{\alpha}$$

With the values extracted from the structural and elasticity analysis, we found $\alpha = 1.9$ and $\tilde{d} = 1.26$.

From the definition of $g(\omega)$, it follows that, in the relevant temperature range, the specific heat per unit of mass is given by : $C_p(T) \sim T^{\tilde{d}}$, which provides the most appropriate determination for $\tilde{d}$. Below 2 K, such a power law has been observed (fig.1.1) and the experimental values δ (table 1) are close from the predicted one. Brillouin /11/ and Raman /6/ scattering can also produce determinations of $\tilde{d}$ which range between 1.18 and 1.25 and are compatible with the previous calculation.

Concerning the thermal conductivity, we suppose that the modes of vibrations at each stage of the hierarchy are not strongly localized (in contrast with the concept of fractons). Then, the kinetic formula for the heat conductivity is :

$$K = \frac{1}{3} \int_0^{\omega_{\max}} g(\omega) E\left(\frac{\omega}{T}\right) V(\omega) L(\omega) d\omega$$

where $E(\omega/T)$ is the Einstein function for the specific heat, $V(\omega)$ the group velocity and $L(\omega)$ the phonon mean free path. Assuming that $L(\omega)$ of the excitations is proportional to the diameter of the rods at the stage n (Casimir regime) :

$$L(\omega) \sim a_n \sim h^n \cdot a_0 \sim \omega^{-1/\alpha}$$

From the anomalous dispersion $\omega \sim k^\alpha$ we can derive the group velocity : $V(\omega) \sim \omega^{1-1/\alpha}$. Combining all these functions of ω one finds :

$$K \sim T^{\tilde{d}+1-2/\alpha}$$

For the values mentioned before, one gets : $K \sim T^{1.2}$ which is very close from the experimental law measured above 2 K. This explanation implies that the phonons of higher frequencies which contribute to the specific heat in the same temperature range, are strongly localized as molecular modes and do not contribute to the thermal conduction.

5 - CONCLUSION

The silica aerogels are probably the first example of a new class of fractal materials founded on a hierarchical structure and they exhibit very unusual low temperature thermal behavior. Their mechanical properties follow scaling laws as a function of density, and the scaling exponents are expressed by the geometrical parameters and by the flexion elastic constants of the constitutive micro-rods of the hierarchical structure. From the same parameters, the spectral density of vibrational excitations is derived in order to explain the thermal properties. This model offers a framework to try to found microscopically the concept of fractons.

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