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STRUCTURAL EFFECTS ON BRILLOUIN SCATTERING FROM SILICA AEROGELS

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Résumé - Après avoir décrit la spectroscopie Brillouin sur les aérogels de silice, nous comparons nos résultats antérieurs à de nouvelles données obtenues sur des aérogels préparés en catalyse basique. La même expression pour la transition phonon-fracton semble rester valable, pourvu que les matériaux soient fractals. Toutefois, il est difficile de donner une conclusion sur la valeur de la dimension spectrale \bar{d} de ces nouveaux échantillons. Des mesures complémentaires, qui paraissent difficiles pour des raisons instrumentales, devront être effectuées sur une série d'aérogels mutuellement auto-similaires.

Abstract - Brillouin scattering spectroscopy on silica aerogels is described. Our previous results on neutrally reacted materials are compared to new data on base catalyzed ones. The same crossover expression seems to remain valid provided the materials are really fractal. A definite conclusion on the spectral dimension \bar{d} will have to wait for measurements on a mutually self similar series of base catalyzed samples, which appear difficult for instrumental reasons.

1 - INTRODUCTION

There is currently considerable interest in observing the vibrations of fractal networks. Real systems are homogeneous at large scales, and can become fractal below a correlation length ξ . In this case, one anticipates phonons at long wavelengths, and a crossover to the so-called "fractons" /1/ as the excitation wavelength approaches ξ . This crossover can be defined by its wavevector $q_{co} = 1/\xi$, and by the associated frequency $\omega_{co} = c_0 q_{co}$, where c_0 is the sound velocity in the asymptotic long wavelength limit. Since fractons are expected to be strongly localized /2/, only scattering techniques are suitable for their observation. In non-crystalline materials, it is not possible so far to determine the inelastic structure factor associated with sound waves by neutron scattering. Only Brillouin scattering of light can be used, and it is fortunate that aerogels can be prepared for which ω_{co} and q_{co} fall into the measurement range of that technique. We have shown /3,4/ that spectra obtained on neutrally reacted silica aerogels can be fitted with a theory based on the effective medium approximation (EMA) /5/. Performing measurements on a mutually self-similar series /6/, we were able to extract from such fits both the fractal dimension D and the spectral dimension \bar{d} of these aerogels. The latter relates the fracton density of states to the frequency, $N(\omega) \propto \omega^{\bar{d}-1}$. Since small angle neutron-scattering measurements have shown that aerogels prepared with base catalysis can be excellent fractals /7,8/, and since they have a fractal dimension D very different from that of neutrally reacted materials, it is of interest to investigate Brillouin scattering in these as well. Furthermore, since fractal base catalyzed samples have very low sound velocities, means to increase the elastic constant of the materials are of interest for spectroscopic reasons, as explained below, and thus results on oxidized samples are also reported.

2 - EXPERIMENTAL TECHNIQUE

In Brillouin scattering, an incident photon of frequency ω_{in} and wavevector \mathbf{q}_{in} is scattered into a photon of frequency ω_{out} and wavevector \mathbf{q}_{out} . In this process, an excitation of frequency ω and wavevector \mathbf{q} is created or annihilated in the scattering medium, according to $\omega_{in} = \omega_{out} \pm \omega$, and $\mathbf{q}_{in} = \mathbf{q}_{out} \pm \mathbf{q}$. The spectrometer geometry defines \mathbf{q}_{in} and \mathbf{q}_{out} , but the eigenmodes that are observed do not need to be plane waves. In general, an eigenmode at frequency ω will contribute to the spectrum if the spatial Fourier

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transform of the corresponding excitation has a component at q . In that case, even if the eigenmodes are very long lived, it is sufficient that they have a limited spatial extent and frequency dispersion to lead to a spectral broadening, which is inhomogeneous. On the opposite, a finite lifetime of the eigenmodes leads to homogeneous broadening of the lineshapes. The difference between the two broadening mechanisms can generally be recognized on the temperature dependence, since temperature has a strong effect on lifetime and a small one on dispersion. In the case of the aerogels, the broadening is inhomogeneous and the excitations have a very long lifetime.

For the frequency shifts of interest in Brillouin scattering, typically of the order of 1 to 50 GHz, the choice spectroscopic technique is Fabry-Pérot interferometry. The classical interferometer suffers from lack of contrast and order overlap. In modern instruments, the former difficulty is overcome by multipassing, while the latter can be avoided in tandem instruments /9/. Both aspects are important in light scattering from aerogels, since it is necessary to discriminate against the strong elastic scattering, and since considerable information is contained in the unusual features of the broad lineshapes which are much better seen without order overlap. We have used in these experiments a six-pass tandem Sandercock interferometer /9/, with a mirror spacing of up to 3 cm, or an order spacing down to 5 GHz. With a finesse close to 100, this implies a resolution close to 50 MHz. With digital data accumulation and careful numerical fitting, spectral widths can be extracted with an accuracy close to 10 MHz.

In Brillouin scattering, q is related to the scattering angle θ by $q = 4\pi n \sin(\theta/2)/\lambda$, where n is the refractive index, which is close to one in the case of aerogels, and λ is the wavelength of the exciting radiation. The maximum q that can be achieved is obtained in backscattering ($\theta = 180^\circ$), and for green light it is $\approx 2.5 \times 10^5 \text{ cm}^{-1}$. This limits the accessible q - ω space to $q < q_{\text{max}}$, as indicated in Fig. 1. Another limitation is that the scattering angle that can be accepted while maintaining the resolution is inversely proportional to $dq/d\theta$. This causes no difficulty in backscattering, but becomes a problem near forward scattering, thus limiting the lowest q to about one tenth of its maximum value. Furthermore, in spite of the high resolution, the rejection of the elastic light becomes poorer as one approaches $\omega = 0$. This imposes a practical lower limit of $\omega \gtrsim 200 \text{ MHz}$ in our experiment. For a meaningful measurement of the phonon-fracton crossover it is important to select samples for which both q_{co} and ω_{co} can be in the accessible range. Note that in the phonon regime, $\omega = c_0 q$, while for fractons $\omega \propto q^{D/d}$, as sketched in Fig. 1. For a successful measurement, it is clearly necessary that the sound velocity be sufficiently large, and that q_{co} be sufficiently small. This does present some problems if one wishes to examine a series of fractal aerogels. Although it was possible to match neutrally reacted gels to these experimental requirements /3,4/, it is more difficult in the case of base catalyzed gels which need to be extremely light, and thus have a very small sound velocity, when they are sufficiently fractal /8/.

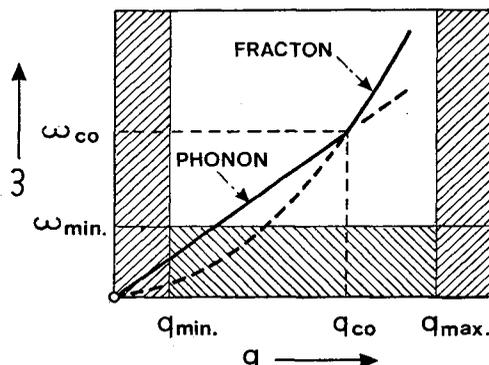


Figure 1 - The accessible experimental range is between q_{min} and q_{max} , and above ω_{min} . Also shown are a phonon and fracton dispersion curve, with crossover, ideally matched to the instrumental capability.

3 - SCATTERING FROM BASE CATALYZED MATERIALS

Brillouin scattering was measured for a few base catalyzed aerogels, in the manner described elsewhere for neutrally reacted ones /3,4/. Spectra have been fitted with the EMA theory of Ref. 5, as explained previously /4/. The scattering formula depends on crossover expressions for the velocity $c(\omega)$ and the linewidth $\Gamma(\omega)$:

$$c(\omega) = c_0 \left[1 + \left(\frac{\omega}{\omega_{co}} \right)^m \right]^{z/m} \quad (1)$$

$$\Gamma(\omega) = g \frac{\omega^4}{\omega_{co}^3} \frac{1}{\left[1 + \left(\frac{\omega}{\omega_{co}} \right)^m \right]^{3/m}} \quad (2)$$

The sharpness of crossover is determined by the exponent m , and there may be a prefactor g of the order of 1 in the expression for the linewidth. The asymptotic exponent of the velocity in the fracton regime is fixed by z . In the analysis of the series of mutually self-similar /6/ neutrally reacted gels /4/, it was found that $m = 2$ and $g = 1$ gave excellent fits to spectra on all samples and at all scattering vectors. Furthermore, the value z could be determined self-consistently, since $z = 1 - \bar{d}/D$, and both D and \bar{d} are found from the scaling in ρ of ω_{co} and q_{co} . Thus, each individual lineshape finally depends only on three freely adjustable parameters, namely ω_{co} , $q_{co} \equiv \omega_{co}/c_0$, and the absolute intensity.

In the case of base catalyzed aerogels B20S and B30S (see Table I), we find that $m = 2$ and $g = 1$ also give satisfactory fits. However, it is not clear which value should be taken for z . With only two samples, which furthermore are likely not to be mutually self-similar as explained below, scaling cannot help in this case. Starting from the EMA value, $z = 0.5$, we find an improvement in the fits as z is increased up to ≈ 0.75 . The fits degrade when z is made smaller than 0.5. From SANS on the lightest sample, we know that $D \approx 1.8$ /7/. A value $\bar{d} \approx 1.3$, as found for the neutrally reacted materials /4/, would then lead to z smaller than 0.5, in disagreement with the observed lineshapes. We conclude that \bar{d} for the base catalyzed aerogel might be much smaller than 1.3, possibly of the order of 0.5. A rather small value happens to be in agreement with a model calculation of the modes in expanded silica /10/. An example of a fit in the fracton regime is shown in Fig. 2 for sample B20S.

In the case of B50S, keeping the value $z = 0.75$, a significant improvement in the fits is obtained by taking $m = 4$ and $g = 0.4$. This is also illustrated in Fig. 2. It is interesting to note in Table I that this material shows hardly any hardening upon oxidation, a very different behavior from that of the other two samples.

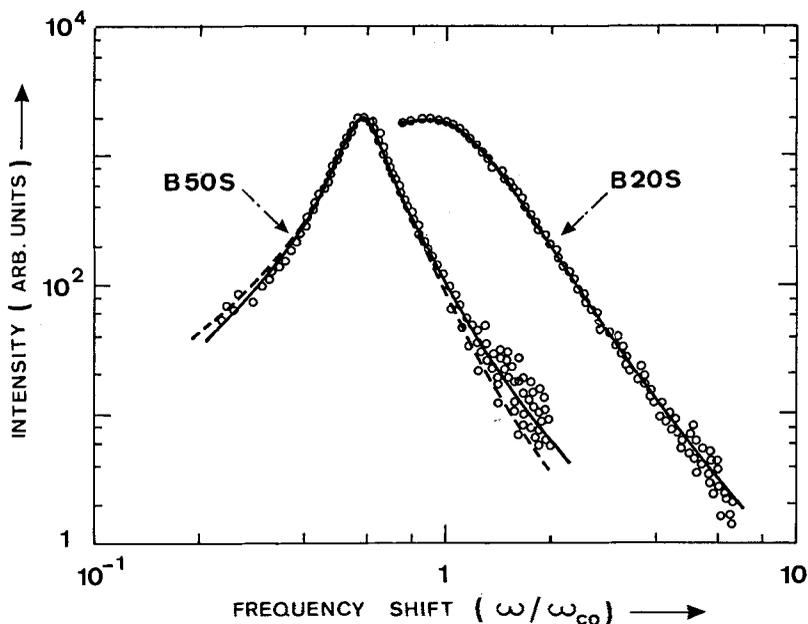


Figure 2. Examples of light-scattering spectra for two base catalyzed and oxidized aerogels. The abscissa scale is normalized to the crossover frequency ω_{co} of each sample, as listed in Table I. The solid line on B20S corresponds to the best fit obtained with $m = 2$, $z = 0.75$, and $g = 1$. The best fit with the same parameters leads to the dashed line for sample B50S. For that sample, a better fit is obtained with $m = 4$ and $g = 0.4$ as shown by the solid line.

Table I - Results obtained on three base catalyzed compositions. The crossover frequencies and sound velocities are derived from an average over measurements at several q -values. Note that $v_{co} = \omega_{co}/2\pi$. The fits from which ω_{co} and c_0 were obtained were performed with $z = 0.75$, and the values of m and g shown in the Table.

Sample	ρ kg/m ³	Non-oxidized		Oxidized		ξ Å	m	g
		v_{co} GHz	c_0 m/s	v_{co} GHz	c_0 m/s			
B50S	200	0.95	225	0.95	230		4	0.4
B30S	140	0.38	110	0.54	150		3	1
B20S	107	0.25	70	0.40	110	~450	2	1

Base catalyzed materials of that relatively high density do not exhibit a convincing fractal region in SANS /7/. This may well be related to the absence of oxidation hardening and to the other parameter values that are needed to fit the spectra. Returning then to sample B30S, a somewhat better fit is found with $m = 3$ instead of $m = 2$; it is for this value of m that the fit results are given in Table I. This suggests that B30S is intermediate in its fractal behavior between B20S which is really fractal, and B50S which is hardly fractal at all.

4 - CONCLUSIONS

As seen above, the spectra on the fractal base catalyzed sample can be fitted with the same values $m = 2$ and $g = 1$ also successful in the case of fractal neutrally reacted samples. The value of g implies that the Ioffe-Regel /11/ and the phonon-fracton crossover frequencies approximately coincide. However, the fairly broad crossover region given by $m = 2$, might indicate a succession of two crossovers which are not taken into account in our fitting expression. One notices that oxidation has a strong effect on both ω_{co} and c_0 on the fractal sample B20S. Remarkably, the value of q_{co} deduced from these parameters remains unchanged within the experimental accuracy, as shown by $\xi = 1/q_{co}$ in Table I. This should be the case, since oxidation only modifies the aerogel at the particle scale. The result gives additional support to the simple crossover model.

The high value obtained for z in the fits is an indication that \bar{d} could be rather small for base catalyzed materials. It would be interesting to be able to verify this on a series of mutually self-similar samples. There is however an important instrumental difficulty, as the crossover frequency for lighter samples will quickly fall below the lower frequency limit imposed by elastic scattering in our apparatus. Oxidation can be a slight help in this context.

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