

## Direct Experimental Determination of the Crossover Frequency between Phonon and Fracton Regimes and its Scaling Behavior in Superionic Silver Borate Glasses

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We determined the crossover frequency  $\omega_{co}$  between phonon and fracton regimes from the study of the low-frequency inelastic light scattering in superionic borate glasses of the type  $(AgI)_x(Ag_2O \cdot nB_2O_3)_{1-x}$ . The scaling of  $\omega_{co}$  with the fractal characteristic length was studied by variation of the AgI concentration  $x$ . We thus obtained the diffusion coefficient scaling exponent  $\theta$  and the spectral dimensionality  $\tilde{d}$  which characterizes energy diffusion on a fractal.

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In recent years the fractal description has been intensively used to treat the microscopic structure and dynamics of inhomogeneous systems.<sup>1</sup> In this Letter we report what we believe is the first direct experimental determination of the scaling behavior of the crossover frequency  $\omega_{co}$  between the phonon and the fracton regimes<sup>2</sup> as a function of the fractal characteristic length  $l_f$ .

We studied the low-frequency ( $2 \text{ cm}^{-1} < \omega < 30 \text{ cm}^{-1}$ ) inelastic light scattering in a particular class of glasses, the superionic borates, as a function of the relative concentration of the active component, AgI.

Superionic borate glasses<sup>3</sup> are mixtures of the binary compound  $Ag_2O \cdot nB_2O_3$  ( $n=1,2,3,4$ ), which provides the host matrix, and AgI, which tends to go inside such matrix in the form of distorted connected tetrahedra.<sup>4</sup> This system turned out to be quite useful for the experimental study of dynamics on fractals, and in fact has already been studied from this point of view by specific heat measurements.<sup>5</sup> However, thermodynamic determinations are only sensitive to the integral of the relevant quantity, namely, the vibrational density of states  $\rho(\omega)$ , and therefore they all must depend to some extent on theoretical input.

In the superionic borate glasses, however, precise determination of the low-frequency Raman spectral density is possible, since they can be produced with reasonably high optical quality and a reasonable transparency in the red part of the spectrum (where the Krypton laser lines may be used). Furthermore, in these glasses a reliable and quantitative separation of the weak Raman scattering from the strong quasielastic scattering present at the low-frequency shifts sampled in the experiment is possible. In fact, the quasielastic contribution has a

definite temperature dependence,<sup>6</sup> which permits its identification mainly as a result of the diffusive motion of the Ag ions belonging to the AgI tetrahedra, and its precise parametrization and subsequent subtraction from the overall scattering.

Therefore such systems are characterized both by a possible fractal behavior and by the potential for precise determination of the low-frequency Raman scattering, which is directly connected with the vibrational density of states  $\rho(\omega)$ .

The samples were prepared in our laboratory, following a technique described in Magistris *et al.*<sup>3</sup> Both density and  $T_g$  (glass temperature) values agreed with those reported in the literature; x-ray diffraction patterns showed no evidence of crystalline peaks. The samples specifically used for this study were  $(AgI)_x(Ag_2O \cdot 1B_2O_3)_{1-x}$  with  $x=0.45, 0.50, 0.55, 0.60, 0.65,$  and  $0.70$ . For all of these the color ranged through various shades of red; they were optically clear and homogeneous.

Raman spectra were taken with a standard system, already described elsewhere.<sup>6</sup> We used the 6471-Å Kr-laser line for excitation, at a nominal power level which was always kept below 100 mW, in order to avoid undue heating of the sample. The spectra were taken down to  $2\text{-cm}^{-1}$  frequency shift, with the use of an instrument resolution of  $0.8 \text{ cm}^{-1}$ . A slowly varying luminescence background was parametrized and then subtracted from the scattered intensity, and finally the quasielastic contribution was evaluated and subtracted, according to the procedures described in Ref. 6. The resulting spectra were then normalized for the Bose-Einstein factor (see following paragraph). These various steps are shown in

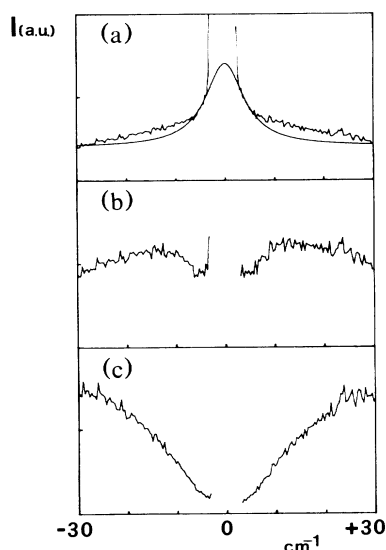


FIG. 1. Low-frequency Raman scattering between  $-30$  and  $+30$   $\text{cm}^{-1}$  for the  $x=0.65$  sample at room temperature. The spectral resolution is  $0.8$   $\text{cm}^{-1}$ . In (a), the solid curve is a Lorentzian best fit to the quasielastic part of the scattering (see Ref. 11 for details); in (b), the Lorentzian has been subtracted from the experimental data; in (c), the resulting spectral density has been normalized by the Bose-Einstein population factor.

Fig. 1; the bottom figure [Fig. 1(c)] shows the final experimental quantity we worked with.

In principle, incoherent inelastic neutron scattering is the most direct way to obtain the frequency-distribution function of any system<sup>7</sup>; for the low-frequency range however, experimental and data handling difficulties have made the determination of  $\rho(\omega)$  difficult and unreliable. To our knowledge, only in one case was  $\rho(\omega)$  determined with sufficient precision to detect small deviations from the  $\rho_{\text{ac}}(\omega) \sim \omega^2$  Debye behavior at low frequencies.<sup>8</sup> Even in this case, however, the deviations were indeed small and no attempt at a crossover analysis was made. Actually, stronger deviations were observed in a precise determination of  $\rho(\omega)$  in liquid water and aqueous solutions of  $\text{ZnCl}_2$ <sup>9</sup>; however, at least for the time being, a fracton interpretation of these data has not been given.

Far infrared and microwave spectroscopy have also been used to study low-frequency excitations in glasses<sup>10</sup>; however, only the Debye phonon behavior was observed.

In a disordered system, the Raman spectral density may be expressed by<sup>11</sup>

$$r(\omega) \sim \int \rho(\omega) C(\omega - \omega') d\omega', \quad (1)$$

where  $C(\omega)$  is the electron-vibration coupling function and

$$R(\omega) = \frac{I(\omega)}{n(\omega, T) + 1} \Gamma(\omega),$$

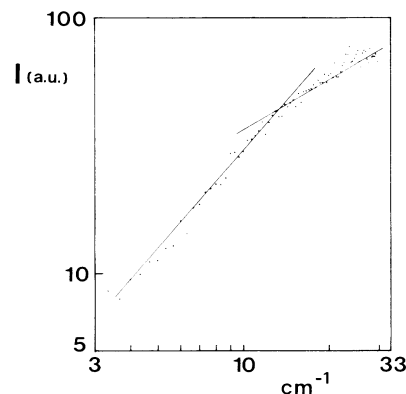


FIG. 2. Log-log plot of normalized Raman spectral density vs frequency shift. The straight lines are least-squares best fits; the two resulting slopes are 1.5 and 0.66, respectively.  $x=0.65$ .

where  $I(\omega)$  is the scattered light intensity,  $n(\omega, T) = [\exp(\hbar\omega/kT) - 1]^{-1}$  is the Bose-Einstein statistical factor and  $\Gamma(\omega) = \omega$  in the harmonic approximation. The convolution (1) simplifies to a sum over vibrational mode "bands" in the decoupling approximation<sup>12</sup>:

$$R(\omega) \sim \sum_i C_i \rho_i(\omega),$$

where now the  $C_i$  are constants. In the low-frequency acoustic region,  $\rho_i(\omega) = \rho_{\text{ac}}(\omega)$ , and  $R(\omega)$  and  $\rho(\omega)$  would be proportional. On general grounds, however, we should expect that in the acoustic phonon range  $C(\omega) \sim \omega^2$ .<sup>13</sup> Experimental confirmation of this is, however, somewhat contradictory and sample dependent.<sup>9,11,14</sup> Given this uncertainty we choose to treat  $C(\omega)$  as a phenomenological coupling function.

In Figs. 2 and 3 we plot (log-log scale) the spectral density  $R(\omega) = I(\omega)/(n+1)$  vs  $\omega$  for some of the samples. The  $x=0.45$  sample spectral density seems to follow a Debye behavior [which would imply that  $C(\omega) = \text{const}$  for this sample]. As  $x$  increases, a clear deviation from such behavior emerges. The Debye region at low frequencies remains; however, its range is restricted by the appearance of the anomalous region, for which the characteristic exponent turns out to be roughly independent on  $x$  and with an average value of  $0.66 \pm 0.07$ . The crossover region itself is clearly identifiable, and its position shifts to lower frequencies with increasing  $x$ . Here we must note that the exponent for the Debye region is not precisely 1, as it is for  $x=0.45$ ; rather it seems to increase as  $x$  increases.<sup>15</sup> Independently of this, the existence of a crossover and its shift with AgI concentration are clearly established by our data.

Let us now turn to a preliminary interpretation. If  $l_f$  denotes the fractal characteristic length (i.e., roughly for  $l < l_f$  we are in the fracton regime and for  $l > l_f$  in the phonon regime), the scaling law for the crossover fre-

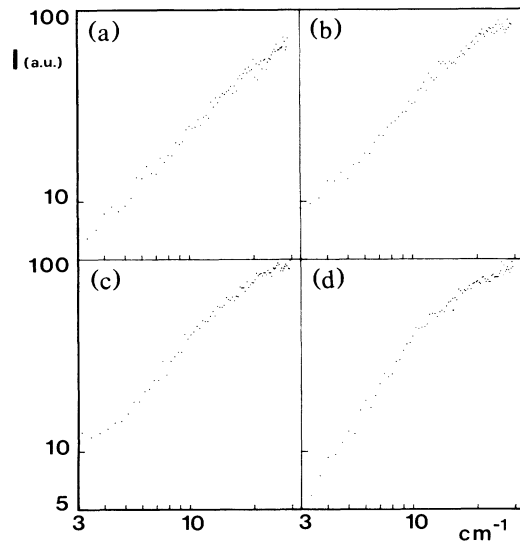


FIG. 3. Log-log plot of normalized Raman spectral density vs frequency shift for several values of AgI concentration: (a)  $x=0.45$ ; (b)  $x=0.50$ ; (c)  $x=0.60$ ; (d)  $x=0.70$ .

quency  $\omega_{co}$  reads<sup>2</sup>

$$\omega_{co} \sim l_f^{-[1+\theta/2]}, \quad (2)$$

where  $\theta$  is the exponent for the length scaling behavior of diffusion on a fractal.<sup>16</sup>  $\theta$  is in turn connected to the spectral dimensionality  $\tilde{d}$  by<sup>2</sup>

$$\tilde{d} = 2D/(2+\theta), \quad (3)$$

where  $D=d_f$  for the infinite cluster in a percolation network and  $D=d$  if finite clusters are also present. In our case  $\tilde{d}$  may be obtained from the anomalous portion of the plots shown in Figs. 2 and 3.

Finally, the crossover frequency may also be obtained from a rescaling of an effective Debye frequency as extrapolated from the actual velocity of sound<sup>2,5</sup>

$$\omega_{co} = (a/l_f)\tilde{\omega}_D, \quad (4)$$

where  $a$  is the shortest length scale for the system. Inverting (4) and with the use of experimentally determined values for  $a$ ,  $\tilde{\omega}_D$ , and the  $\omega_{co}$  values obtained here, we arrive at a value for  $l_f$ . For  $a$  we have used the Ag-I distance values as determined at the relevant  $x$  concentrations by extended x-ray-absorption fine structure (Dalba *et al.*,<sup>4</sup> and unpublished results). The corresponding values of  $\tilde{\omega}_D$  were obtained with the use of the longitudinal and transverse sound velocities (Carini *et al.*<sup>4</sup>) with use of formula (3) in Ref. 5. The results for  $\omega_{co}$  and  $l_f$  are shown in a log-log plot in Fig. 4. From the slope of the best-fit straight line we obtain  $\theta = 2 \pm 0.3$  for the diffusion scaling exponent. It is interesting to note that such value is reasonably close to the theoretical prediction ( $\theta=1.5$ ) for diffusion on a three-dimensional

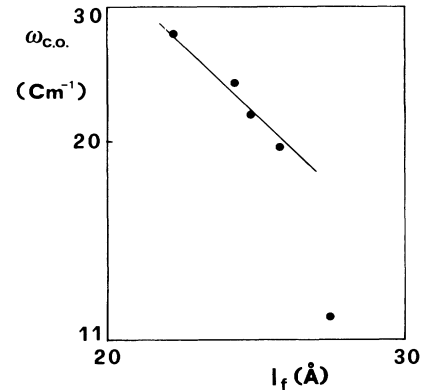


FIG. 4. Log-log plot of the crossover frequency  $\omega_{co}$  vs the fractal characteristic length  $l_f$ . The slope of the best-fit straight line is  $2 \pm 0.3$ .

percolation cluster.<sup>16</sup> However, we must also note that our value for  $\theta$  is only qualitative, given the small number of points in the plot of Fig. 4, and the necessity of using many other independently determined physical quantities.

The form of the vibrational spectral density shows no sharp rise<sup>17</sup> in the neighborhood of  $\omega_{co}$ , nor does it show the bump predicted if bond-bending vibrations were contributing most of the density of states in this range.<sup>18</sup> Rather, it features a smooth crossing over to the fracton regime, characterized only by one length  $l_f$ , over which the longitudinal-bond stretching contribution is dominant.

In order to obtain  $\tilde{d}$  from our data some form of  $C(\omega)$  must be postulated. Given the preliminary nature of our observations it does not seem appropriate at this time to enter into a detailed discussion of electron-vibration coupling. In any case, the  $C(\omega) \sim \omega^2$  dependence expected for the acoustic region should rescale as<sup>19</sup>

$$C(\omega) \sim \omega^{2\tilde{d}/d}, \quad (5)$$

which leads to the fracton region exponent  $m$ <sup>20</sup>

$$m = 2\tilde{d}/d + \tilde{d} - 2. \quad (6)$$

From our experimental value of 0.66 for  $m$  we then obtain  $\tilde{d}=1.66$ , a value which is remarkably close to the one ( $\tilde{d}=1.5$ ) obtained by use of the measured value of  $\theta$  and Eq. (3). Furthermore,  $\tilde{d}=1.66$  is also close—within the experimental error—to the value 1.42 which is predicted for a percolating network at  $d=3$ .<sup>2</sup>

In conclusion, we have determined experimentally for the first time the scaling exponent  $\theta$  in a real system, the superionic borate glasses, for which in turn we show that the AgI dissolved in the host matrix can be described as a three-dimensional percolating network containing both the infinite cluster and finite clusters. The fractal correlation length  $l_f$  turns out to increase from about 20 to 30

Å with AgI concentration.

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