

## Relation of structural and elastic crossover length investigated by low-frequency Raman scattering in $\text{Ge}_x\text{Se}_{1-x}$ glasses

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Low-frequency Raman spectra ( $10\text{ cm}^{-1}$ – $80\text{ cm}^{-1}$ ) have been studied in the  $\text{Ge}_x\text{Se}_{1-x}$  ( $0.02 \leq x \leq 0.40$ ) glasses. The Raman spectra reduced by the Bose factor  $I_R(\omega)$ , which are proportional to the vibrational density of states, show a power-law dependence of the frequency,  $\omega$ ,  $g(\omega) \propto \omega^{\bar{d}-1}$  in a low-frequency region. The value  $\bar{d}$  is a noninteger, which suggests that these glassy systems have fractal structures. The spectra  $I_R(\omega)$  of Se-rich samples are classified into three regions whose vibrational properties are due to acoustic phonons, bending fractons, and stretching fractons, whereas that of the Ge-rich samples' two regions are due to acoustic phonons and stretching fractons. The difference of two types of these low-frequency properties are explained by correlation of the *structural* crossover length  $\xi$  and the *elastic* crossover length  $l_c$ . The threshold of these phenomena occurs near  $\langle r \rangle \sim 2.4$ , which may be related to the prediction of the Phillips-Thorpe constraint theory. [S0163-1829(98)10017-6]

Low-energy excitations in disordered materials presents universal features such as a plateau in their low-temperature thermal conductivity and an appearance of a Boson peak in Raman and inelastic neutron-scattering spectra. A great many works have been devoted to attain a complete picture of the low-energy dynamics. These important and interesting subjects, however, is not yet resolved. In this paper, we tackle this problem with Raman-scattering measurements and the concept of fracton dynamics.<sup>1</sup> Over the decade numerous investigations on dynamics of fractal networks have been made aiming at the understanding of the nature of random systems.<sup>2</sup> The extensive experimental investigations of Raman scattering from fractal structure have been carried out on aerogels.<sup>3,4</sup> Besides studies on aerogels, low-frequency Raman properties of disordered materials have been reported for polymers, such as polymethylmetacrylate (Ref. 5) and glasses, such as borate glass<sup>6</sup> or amorphous arsenic.<sup>7</sup> Theoretical works for Raman scattering from fractal structures are also vigorously made.<sup>8,9</sup>

We present the investigation of the low-frequency Raman properties of  $\text{Ge}_x\text{Se}_{1-x}$  glasses. The  $\text{Ge}_x\text{Se}_{1-x}$  glasses that show a wide range glass-forming tendency ( $0 \leq x \leq 0.42$ ) are easily prepared by quenching the melt in iced water. In the  $\text{Ge}_x\text{Se}_{1-x}$  glasses, the bonding between atoms are mainly covalent, and moreover, the masses of germanium and selenium atoms are almost the same. The  $\text{Ge}_x\text{Se}_{1-x}$  glasses are thought to be an ideal covalent network system for studying the network structure. By changing the germanium contents  $x$ , one can control the structure of the glass and the average coordination number,  $\langle r \rangle = 4x + 2(1-x)$ . At small  $x$ , the glass has a one-dimensional-like network structure mainly composed of Se chains. At the stoichiometric composition  $\text{GeSe}_2$ , the glass has layered two-dimensional-like fragments.<sup>10</sup> The Raman-scattering measurements were made with a triple monochromator (Jobin-Yvon T64000) equipped with a charge-coupled device detector. The wavelength of the excitation light was 632.8 nm of He-Ne laser and the laser power was so low that the photoinduced change should be avoided.

In glassy systems, the intensity of Raman scattering  $I(\omega)$  at the frequency  $\omega/2\pi$  is usually written in the form<sup>11</sup>

$$I(\omega, T) = C(\omega)g(\omega)[n(\omega, T) + 1]/\omega, \quad (1)$$

where  $n(\omega, T) + 1$  is the Bose factor for the Stokes scattering,  $g(\omega)$  the vibrational density of states (VDOS), and  $C(\omega)$  the coupling between the light and lattice vibration. The function  $C(\omega)$  can be determined by comparison of inelastic neutron- and Raman-scattering spectra. It has been found that  $C(\omega) \propto \omega$  for disordered materials of various types.<sup>12</sup> This relation holds in the low-frequency region above the Boson peak position. By taking into account a relation of  $C(\omega) \propto \omega$ , Raman intensity reduced by the Bose factor  $I_R(\omega)$  is proportional to VDOS in the low-frequency region and is independent of temperature,

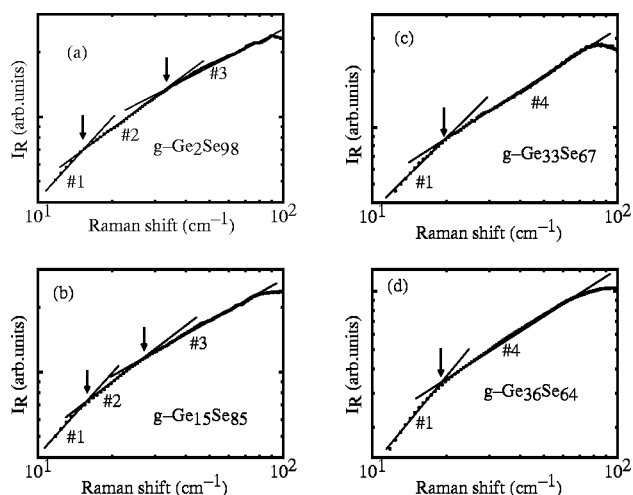


FIG. 1. The log-log plots of reduced Raman spectra  $I_R(\omega)$  of  $\text{Ge}_x\text{Se}_{1-x}$  glasses in the low-frequency region. The spectrum of the Se-rich sample (a),(b) is fitted by three straight lines, while that of the Ge-rich sample (c),(d) is fitted by two straight lines.

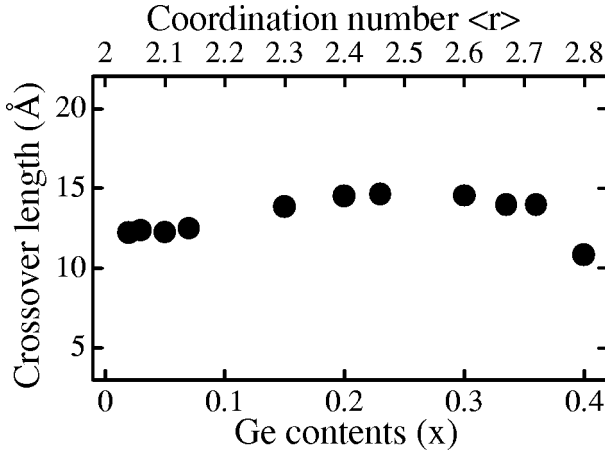


FIG. 2. The estimated structural crossover length  $\xi$  of  $\text{Ge}_x\text{Se}_{1-x}$  glasses.

$$I_R(\omega) \equiv \frac{I(\omega, T)}{n(\omega, T) + 1} \propto g(\omega). \quad (2)$$

We refer to a certain  $\omega$  dependence of VDOS,  $g(\omega) \propto \omega^{\bar{d}-1}$ , as a fracton behavior.<sup>1</sup> The value of  $\bar{d}$ , which is referred to as spectral dimensionality, is not an integer.

Figure 1 shows the log-log plots of the reduced Raman spectra  $I_R$  of the  $\text{Ge}_x\text{Se}_{1-x}$  glasses. For the Se-rich samples ( $x=0.02, 0.15$ ), each spectrum is fitted by three kinds of straight lines and for the Ge-rich samples ( $x=0.33, 0.36$ ) by two kinds of straight lines. It is considered that the line #1 represents the Debye behavior [ $g(\omega) \propto \omega^2$ ] and lines #2–#4 correspond to the fracton behavior. The slope of line #1, however, is not an integer value. It may be due to the  $\omega$  dependence of  $C(\omega)$  that is no longer proportional to  $\omega$  in the very low-frequency region below the Boson peak position.

By using the sound velocity data of these glasses, the structural correlation length  $\xi$  can be estimated from the point at which #1 and #2 (or #4) lines cross. Figure 2 shows the estimation of the correlation length  $\xi$  of  $\text{Ge}_x\text{Se}_{1-x}$  glasses by using the following expression:

$$\xi = Sv_t / \omega_0, \quad (3)$$

where  $v_t$  is the transverse sound velocity and  $\omega_0$  the frequency #1 line and #2 or #4 line crosses. A shape factor  $S$  depends on the cluster shape. For a spherical shape  $S \cong 0.8$ , and 0.5 for a linear shape. In the case of a sphere,  $\xi$  is the diameter, and the length for a line. Without knowing the cluster shape, we will take a mean value  $S = 0.65$ .<sup>12,13</sup> The data of transverse sound velocity are referred to in the literature.<sup>14</sup> Thus obtained correlation lengths  $\xi$  of  $\text{Ge}_x\text{Se}_{1-x}$  glasses are in the range of 10–15 Å. Above the length  $\xi$ , the structure is regarded as homogeneous, while below  $\xi$ , the structure is considered to be inhomogeneous or fractal.

Next we consider the reason why the log-log plot of the reduced Raman intensity is fitted by two or three straight lines depending on the composition ratio. We shall discuss two kinds of low-frequency properties in terms of vector elasticity.<sup>15–18</sup> It has been pointed out that the vector nature of atomic displacement is essential for describing the fracton

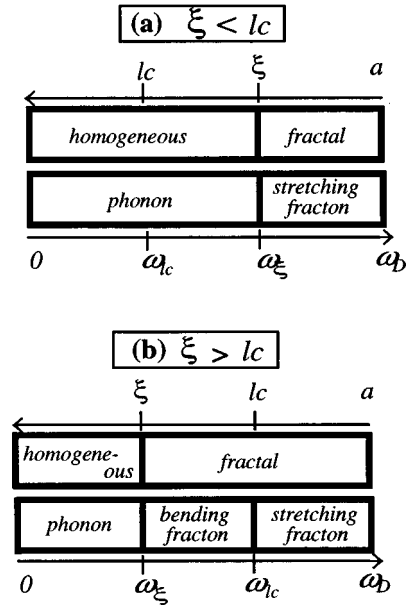


FIG. 3. Schematic diagram showing the correspondence between length scales and frequencies (after Ref. 15). (a) In the case of  $\xi < l_c$ , vibrational excitations in a low-frequency region are acoustic phonons and stretching fractons. (b) In the case of  $\xi > l_c$ , they are acoustic phonons, stretching fractons, and bending fractons.

excitation in real materials. In the vector elasticity model, the potential energy is given by<sup>15–17</sup>

$$V = \frac{1}{2} \alpha \sum_{\langle ij \rangle} g_{ij} [(\mathbf{u}_i - \mathbf{u}_j) \cdot \mathbf{r}_{ij}]^2 + \frac{1}{2} \beta \sum_{\langle ijk \rangle} g_{ij} g_{ik} (\delta\theta_{jik})^2. \quad (4)$$

Here,  $\mathbf{u}_i$  is the vector displacement of atom  $i$ ,  $\mathbf{r}_{ij}$  the directional unit vector between nearest neighbors  $\langle ij \rangle$ ,  $\delta\theta_{jik}$  is the change in the angle between bond  $\langle ij \rangle$  and  $\langle ik \rangle$  due to the displacements of atoms;  $g_{ij} = 1$  for the bonds that are occupied and  $g_{ij} = 0$  for the bonds that are empty, and  $\alpha$  and  $\beta$

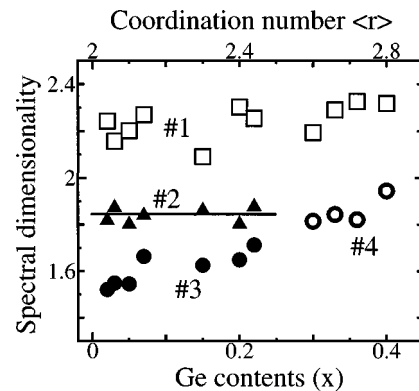


FIG. 4. The spectral dimensionalities obtained by the slope of the lines (#1–#4). The data of #1 are supposed to correspond to Debye behavior. The data of #2 are due to the bending fracton and those of #3 and #4 are due to the stretching fracton.

are the bond stretching and bond bending force constants, respectively.

We suppose that two crossover lengths  $\xi$  and  $l_c$  independently exist in the Ge-Se network glass as discussed in the following. The length  $\xi$  is the *structural* crossover length, which was mentioned above. We take a characteristic length of interest as  $L$ , for example the wavelength of the excitation. When the relation of  $L > \xi$  holds, the structure is regarded as homogeneous. A vibrational excitation whose wavelength equals  $L$  belongs to extended modes (acoustic phonons). In the case of  $L < \xi$ , the structure is considered to be fractal, and a vibrational excitation of wavelength  $L$  is strongly localized (fracton). The length  $l_c$  is the *elastic* crossover length where the bond stretching motion is energetically favorable ( $L \ll l_c$ ) or the bond bending motion becomes dominant ( $L \gg l_c$ ). This crossover length  $l_c$  is determined from the ratio between the bond bending force constant  $\beta$  and the bond stretching force constant  $\alpha$  as  $l_c \propto (\beta/\alpha)^{1/2}$ .<sup>15,16</sup> When  $\xi < l_c$ , the low-frequency vibrational properties are dominated by acoustic phonon and stretching fracton as shown in Fig. 3(a). This situation corresponds to the case of the Ge-rich samples. On the other hand, in the case of  $\xi > l_c$ , the bending fracton contributes to the low-frequency vibrational properties besides acoustic phonon and stretching fracton as illustrated in Fig. 3(b). This relation causes the low-frequency properties of the Se-rich samples. Accordingly, the origins of #3 and #4 straight lines are both due to stretching fracton modes.

As shown in Fig. 4, the spectral dimensionalities of bending fractons  $\tilde{d}_b$  (#2) have almost constant value, whereas those of stretching fractons  $\tilde{d}_s$  (#3 and #4) linearly increase with the germanium contents. In all cases, the relation  $\tilde{d}_{b,s} < 2$  holds, which is a condition where excitations are localized. It is noteworthy that the relation of  $\tilde{d}_b > \tilde{d}_s$  is realized at any composition. This relation contradicts a prediction by a scaling analysis for a percolating network, which results in  $\tilde{d}_b < \tilde{d}_s$ .<sup>17,18</sup> Explaining these experimental results will be still a challenging problem. When we take  $C_{b,s}(\omega)g_{b,s}(\omega) = \omega^{\nu_{b,s}} [g_{b,s}(\omega) = \omega^{\tilde{d}_{b,s}-1}]$ , the axis of ordinates for Fig. 4 is the value of the  $\omega$  exponent  $\nu_{b,s}$  in practice. So far, we have taken the relation that  $C(\omega)$  is proportional to  $\omega$ . One possibility is that the difference of the  $\omega$  dependence of  $C(\omega)$  causes the relation of  $\nu_b > \nu_s$  under the condition of  $\tilde{d}_b < \tilde{d}_s$ . For scalar elasticity, the coupling coefficient without coherence is described by the following expression:

$$C_s(\omega) \propto \omega^{2\tilde{d}_s\sigma/D_f - \tilde{d}_s}, \quad (5)$$

where  $D_f$  is Hausdorff fractal dimensionality and the distance  $r$  in the Euclidean space corresponds to  $r^\sigma$  in the fractal space ( $\sigma > 1$ ).<sup>9</sup> We consider that the increase of the value of  $\nu_s$  with the germanium content corresponds to the linear increase of the value of  $\sigma$  with the germanium contents.

At present, we assume that the coupling coefficient for the bending motion is simply described by the following expression:

$$C_b(\omega) \propto \omega^{2\tilde{d}_b/D_f}. \quad (6)$$

Accordingly, the value of  $\nu_b$  holds constant under the  $\omega$  dependence of  $C_b(\omega)$ . Taking the appropriate value for  $\sigma$  and  $D_f$ , the relation of  $\nu_b > \nu_s$  and localization condition,  $\tilde{d}_{b,s} < 2$  hold. The difference between  $C_b(\omega)$  and  $C_s(\omega)$  may depend on an interaction propagating either in the Euclidean space or in the fractal space.<sup>8</sup> The experimental result of  $\nu_b > \nu_s$ , however, leaves room for a variety of interpretations.

Phillips and Thorpe presented the notion of the rigidity percolation in covalent glasses.<sup>19</sup> They developed a mean-field theory for the number of zero-frequency modes in a covalent network glass. Taking into account the constraints by bond-stretching  $\alpha$  and bond bending  $\beta$  forces, rigidity percolation threshold exists in  $\langle r \rangle = 2.4$ .

For  $\langle r \rangle > 2.4$ , the rigid regions percolate in the glass (overconstrained). For  $2 < \langle r \rangle < 2.4$ , the floppy regions percolate in the glass (underconstrained) and the network can be deformed at no cost in energy. The chalcogenide glasses of the type Ge-(As)-Se are a physical realization of rigidity percolation problem because of the weakness of the energy associated with the dihedral angle.<sup>20-25</sup>

In our experiment, the spectral dimensionality of the bending fractons extends to  $\langle r \rangle = 2.44$ , which gives a similar result to Boolchand and co-worker's claim.<sup>22</sup> They claimed that the rigidity threshold in Ge-Se glasses occurs at  $\langle r \rangle = 2.46$ . However, Wang *et al.*<sup>23</sup> and Taniguchi *et al.*<sup>24</sup> reported that the rigidity threshold occurs at  $\langle r \rangle = 2.40$  or less based on their experimental result. Wang *et al.* investigated the temperature dependence of the structural changes in Ge-Se glasses by Raman scattering. Taniguchi *et al.* investigated the valence-band ultraviolet photoemission spectroscopy and conduction-band inverse-photoemission spectroscopy spectra of Ge-Se glasses. In our paper, taking some experimental results into consideration, we only pointed out that the rigidity threshold in Ge-Se glasses occurs "near"  $\langle r \rangle = 2.40$ .

Recently, Phillips discussed the relation between  $\beta/\alpha$  ratio and the constraint theory of network glass<sup>26</sup> to explain the Uebbing and Sievers' data<sup>25</sup> for the relaxation rate  $\gamma$  of the H<sub>2</sub>O symmetrical stretching mode. For  $\langle r \rangle > 2.4$ ,  $\beta$  bending constraints have been replaced by  $\alpha$  stretching constraints, which causes an increase in the concentration of the  $\alpha$  localized mode. In our experimental data in Fig. 4, the contribution of the bending motion seems to vanish in overconstrained glasses, which seems to reconcile his arguments.

In summary, the low-frequency Raman scattering observed for germanium selenide glasses has been discussed in terms of fracton dynamics and the notion of rigidity percolation. The excited vibrational modes of Ge<sub>x</sub>Se<sub>1-x</sub> glasses in the low-frequency region are acoustic phonon and fracton. Especially, the contribution of the bending fracton to the low-frequency region appears only in the underconstrained glasses. We have discussed these phenomena using the concept of the vector elasticity.

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