RAMAN-BRILLOUIN LIGHT SCATTERING DETERMINATION OF THE STRUCTURAL CORRELATION RANGE IN GeS₂ GLASS*

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Polarized Brillouin and low frequency $(3 \text{ cm}^{-1} \le \omega \le 40 \text{ cm}^{-1})$ Raman spectra of GeS₂ glass have been measured. Parameters determined from the Brillouin spectra have been used in the theory of Martin and Brenig to obtain from a fit of the Raman spectrum the structural correlation range, 2σ . We find $2\sigma = 8 \pm 1$ Å.

ONE of the key parameters which characterizes the structure of a disordered solid is the structural correlation range (SCR), the characteristic length within which the positions of atoms in an amorphous solid are correlated. Only recently, however, have definitive experimental procedures for determining the SCR been proposed. Most noteworthy in this regard is the work of Martin and Brenig (MB).¹ They have carefully established a theoretical basis for a straightforward experimental determination of the (SCR) from the low frequency light scattering spectrum of a disordered solid. Yet the MB theory remains largely untested. Thus we have undertaken a thorough examination of the low frequency light scattering spectra of several bulk glass compounds and alloys formed from Ge, As, S and Se. The complete details and results of that examination will be reported elsewhere.² In this communication we shall focus on GeS₂ as a model compound to which the MB theory can be applied. Our purpose is to compare the low frequency light scattering results for the SCR with the results of other techniques such as X-ray diffraction and normal ($\omega \ge 30 \text{ cm}^{-1}$) Raman scattering. The MB model can also be used to calculate the low frequency depolarization spectrum of a disordered solid. Therefore, as an additional test of the model, the theoretical and experimental polarization properties of the Raman spectra of GeS₂ glass will be compared.

A sample of GeS_2 obtained from G. Lucovsky was a

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rectangular parallelepiped polished on the four large faces. The sample was of high optical quality and exhibited a polarization extinction in excess of 25 dB when placed between crossed polarizers and measured with 6471 Å Kr radiation. The reflectivity, R, of the GeS₂ glass was measured at 5145 Å as was the absorption coefficient, α , which was found to be 0.094 cm⁻¹. The negligibly small value of α allows the index of refraction, n, to be determined solely from the reflectivity as $n = (\sqrt{R} + 1)/(\sqrt{R} - 1)$. We find that R = 0.120 and n = 2.060. This value of n agrees well with the value 2.04 determined from the high frequency dielectric constant.⁴

Transmission right angle Raman measurements of the low frequency $(3 \text{ cm}^{-1} \le \omega \le 40 \text{ cm}^{-1})$ light scattering from GeS₂ glass were performed with a conventional spectrometer but using a very high resolution of 0.6 cm⁻¹. The spectra were excited with the 7525 Å Kr ion laser line. The depolarization spectrum $\rho(\omega)^5$ was obtained from $\rho(\omega) = I_{\parallel,\perp}(\omega)/I_{\perp\perp}(\omega)$ where $I(\omega)$ is the spectral distribution of Raman intensity, ω is the Raman shift in wavenumbers, and the subscripts indicate that incident (scattered) radiation was polarized (analyzed) either parallel to (||) or perpendicular to (1) the scattering plane.

Polarized Brillouin spectra of GeS_2 glass were excited with the 5145 Å line of an argon ion laser operating in single frequency and were recorded in the right angle transmission scattering geometry using a piezoelectrically scanned triple pass Tropel Model 350 Fabry Perot interferometer modified to accommodate Burleigh Model RC 22 corner cubes and Burleigh Model RC70-B4 2 in. mirrors. A photon counting detection system was used in conjunction with a homemade multichannel analyzer to record spectra obtained in the multiscan mode. The interferometer was calibrated by a method described by Grimsditch and Ramdas⁶ with several lines of Ne and Hg spectral lamps. Scanning nonlinearities introduce a slight distortion of the abscissae of Brillouin spectra presented here. However, those nonlinearities

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Fig. 1. Polarized Brillouin spectra of GeS₂ glass recorded in the right angle scattering geometry with a free spectral range of 1.39 cm⁻¹. The transverse (longitudinal) phonons are labeled by T(L).

have been accounted for in the reported values of the Brillouin shifts.

We shall now determine the SCR of GeS₂ glass using the elastic continuum model of MB for low frequency light scattering in disordered solids. From the MB theory it can be shown that the intensity $I_{\parallel,\perp}(\omega)$ of mechanically and electrically disorder induced low frequency light scattering is given by

$$\frac{I_{\parallel,\perp}}{\omega[n(\omega)+1]} = A\omega^2[2g_L(\omega) + 3g_T(\omega)] \qquad (1)$$

where

$$g_L(\omega) = \exp\left(\frac{-4\pi^2 c^2 \omega^2 \sigma^2}{v_L^2}\right)$$
(2)

$$g_T(\omega) = \left(\frac{v_L}{v_T}\right)^5 \exp\left(-\frac{4\pi^2 c^2 \omega^2 \sigma^2}{v_T^2}\right).$$
(3)



Fig. 2. Polarized low frequency Raman spectra of GeS_2 glass recorded with a spectral slit width of 0.6 cm^{-1} . Note that the abscissa is marked in wavenumbers but is linear in wavelength.

Here 2σ is the SCR, $n(\omega)$ is the Bose occupation number, ω is the Raman shift in wavenumbers, $v_T(v_L)$ is the velocity of transverse (longitudinal) sound waves in the glass and A is a constant. Equation (1) is valid when there is no contribution to the scattered intensity at ω from the Brillouin spectral components and in the long wavelength limit defined by

$$x = 2\pi c \left(\frac{\omega}{v_{\mu}}\sigma\right) < 1 \quad \mu = T, L.$$
 (5)

The low frequency depolarization spectrum of a disordered solid can also be deduced from the MB theory and is given by

$$\rho(\omega) = \frac{I_{\parallel,\perp}(\omega)}{I_{\perp,\perp}(\omega)} = \frac{1 + \frac{2}{3} \left(\frac{g_L(\omega)}{g_T(\omega)}\right)}{\frac{4}{3} + \frac{g_L(\omega)}{g_T(\omega)} \left[10 \frac{C_L^2}{C_T^2} + \frac{8}{9}\right]}.$$
 (6)

Here C_{μ} , $\mu = T$, L, are related to the elasto-optic constants P_{ij} and the static susceptibility χ_0 by

$$C_L = 4\chi_0 [P_{44} + \frac{2}{3}P_{12}]$$
 and $C_T = 8\chi_0 P_{44}$ (7)

and equation (6) is based on the assumption that the fractional mean square spatial fluctuations of C_L and C_T , $\delta C_L^2/C_L^2$ and $\delta C_T^2/C_T^2$ respectively are approximately equal. The ratio C_L/C_T can be deduced from the ratio P_{44}/P_{12} which in turn can be obtained from the ratio of

the intensities I_L and I_T , respectively of the longitudinal and transverse phonons in the Brillouin spectrum.

$$\left(\frac{P_{44}}{P_{12}}\right)^2 = 2\left(\frac{I_T}{I_L}\right)\left(\frac{v_T}{v_L}\right)^2 \tag{8}$$

To determine the SCR we first measure the parameters v_L , v_T , and (C_L/C_T) using the Brillouin spectrum. The sound velocities are then used with equation (1) to fit the low frequency disorder induced spectrum with σ as an adjustable parameter. Finally the sound velocities together with C_L/C_T are used with equation (6) to compare the theoretical frequency dependence of the depolarization spectrum with experimental results.

The polarized Brillouin spectra of bulk GeS₂ glass are shown in Fig. 1. As expected⁷ The longitudinal acoustic phonon appears only in $I_{\perp,\perp}$ whereas, the transverse phonon is present only in $I_{\perp,\parallel}$. From the Brillouin shifts of 0.564 and 0.330 cm⁻¹ and the measured index of refraction n = 2.060 we find from the equation for right angle Brillouin scattering

$$v_{\mu} = \frac{c\omega_{\mu}\lambda_{0}}{\sqrt{2n}} \quad \mu = T, L \tag{9}$$

that $v_L = 2.99 \times 10^5$ cm/sec and $v_T = 1.75 \times 10^5$ cm/sec. [In equation (9) λ_0 is the free space wavelength of the incident ratiation.] From the observed relative intensity $I_T/I_L \approx 0.025$ and equations (7) and (8) we also find that $C_T/C_L \approx 3.5$.

The polarized low frequency Raman spectra $I_{1,1}(\omega)$ and $I_{\parallel,1}(\omega)$ of GeS₂ glass are shown in Fig. 2. Note from that figure that GeS_2 like SiO_2^8 exhibits a light scattering excess at low frequencies. This excess and its temperature dependence are addressed elsewhere.² The reduced Raman spectrum $[I_{\parallel,1}(\omega)]/(\omega[n(\omega)+1])$ is plotted in digital form in Fig. 3(a) and is denoted by the solid dots. Also shown as a solid line in Fig. 3(a) is the best computer fit to the data using equation (1)with A and σ as adjustable paarmeters. Only the frequency region of the long wavelength limit defined by equation (5) has been fit. For GeS₂ glass we find $2\sigma =$ 8 ± 1 Å. For $\omega < 5$ cm⁻¹ the experimental spectrum is dominated by the above referenced excess scattering as well as by the Rayleigh and parasitic scattering which of course are not included in the MB model.

The radial distribution function (RDF) of GeS_2 has been reported by Rowland *et al.*⁹ who observed correlations extending to 8 Å, the experimental cutoff. However, there is, to our knowledge, no established procedure for extracting the SCR from an RDF since the point at which oscillations (indicative of correlation) cease depends largely on experimental technique. deNeufille *et al.* have suggested that a correlation range *L* might be inferred from the first peak in the X-ray diffractometer profile of a disordered solid through the



Fig. 3. (a) Comparison of the theoretical reduced Raman spectrum of amorphous GeS_2 (solid line) with the measured spectrum (solid dots). (b) Comparison of the theoretical depolarization spectrum of GeS_2 glass (solid line) with the measured spectrum (solid dots).

Scherrer formula $L = 0.9\lambda/[B(2\theta) \cos \theta]$. Here λ is the X-ray wavelength, $B(2\theta)$ is the width of the peak and θ is its angular position. If the X-ray data of Rowland *et al.* are analyzed in this way one finds $L \approx 13$ Å in reasonable but not exceptional agreement with the SCR of 8 ± 1 Å. Additional information on structural correlations in GeS₂ glass can be extracted from the normal ($\omega \ge 30 \text{ cm}^{-1}$) Raman spectrum which like the spectrum of GeSe₂ shows evidence of vibrational excitations of large symmetric ring structures consisting of six Ge atoms interconnected by S-atoms.¹¹ The first neighbor distance in GeS₂ glass of 2.2 Å yields a ring diameter of 7.3 Å which is in excellent agreement with our observed value of the SCR.

Consider now the experimental depolarization spectrum $\rho(\omega)$ of GeS₂ which is compared in Fig. 3(b) with the corresponding theoretical spectrum calculated using equation (6). The experimental values of $\rho(\omega)$ are much greater than the ratio of the Brillouin intensities $I_{\perp,\parallel}/I_{\perp,\perp} = I_T/I_L = 0.025$. Thus the Brillouin "wing" contribution to the low frequency Raman spectrum is indeed negligible as assumed in the derivation of equations (1) and (6). Nevertheless there is a clear discrepancy between the theoretical and observed depolarization

spectra. Winterling⁸ recently reported that the observed low frequency depolarization spectrum of SiO₂ was frequency independent with $\rho(\omega) = 0.030 \pm 0.03$ in agreement with the $\omega = 0$ value calculated using equation (6). However if the ω dependence of equation (6) is not ignored the theoretical value of $\rho(\omega)$ is 0.23 for x = 0.5[see equation (5)] and 0.12 for x = 1. Thus the theoretical and experimental values of $\rho(\omega)$ are in disagreement for fused SiO₂ as well as GeS₂ glass.

While the MB theory yields through equation (1) a quite reasonable value for the SCR it gives using equation (6) unacceptable values of $\rho(\omega)$. The key distinction between equations (1) and (6) is that the derivation of the latter included the assumption that $\delta C_L^2/C_L^2 \approx \delta C_T^2/C_T^2$. The proper form of equation (6) unencumbered by that particular assumption is obtained merely by

making the following substitution for the term in square brackets

$$\left(\frac{10C_L^2}{C_T^2}\right) \rightarrow \left(\frac{10C_L^2}{C_T^2}\right) \frac{\left[\frac{\delta C_L^2}{C_L^2} + \frac{\delta E^2}{E^2}\right]}{\left[\frac{\delta C_T^2}{C_T^2} + \frac{\delta E^2}{E^2}\right]}$$

where E is the elastic constant. With the proper form of equation (6) and our polarization results we find that $\delta C_L^2/C_L^2 \ll \delta C_T^2/C_T^2$ for GeS₂ glass. Given the multitude of assumptions inherent in the derivation of equation (1), it is not clear whether the condition $\delta C_L^2/C_L^2 \ll \delta C_T^2/C_T^2$ is alone responsible for the discrepancy between the theoretical and experimental values of the depolarization ratio.

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