Low-frequency Raman investigation of the liquid-glass transition in glycerol

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The low-frequency response of glycerol has been studied by polarized Raman scattering. The "boson peak" always appear far above $T_g = 193$ K, whereas the depolarization ratio is nearly constant between 5 cm^{-1} and 200 cm^{-1} at temperatures from 333 to 90 K. In the analysis of the boson peak, comparisons are made between experimental results and calculations based on the two types of structural correlation function. The typical behavior of line shape and depolarization ratio of the spectra is fitted with an exponential structural correlation function. The structural correlation length is estimated to be about 14 Å. It may be associated with the mean size of the clusters of hydrogen-bonded molecules.

I. INTRODUCTION

The low-frequency Raman spectrum of the liquid-glass transition has never been satisfactorily understood. In amorphous materials, most Raman spectra have shown a low-frequency response, called the "boson peak" and it has been mostly analyzed by the Martin-Brenig model (MB).[1] In the model boson peak is calculated from the density of states of the acoustic phonon and the Gaussian structural correlation function. In the region higher than the boson peak, however, the calculation shows great deviation from the experimental results. For the better fitting of the higher region, an exponential correlation function or a log-normal size distribution of clusters has been considered.[2-3]

The depolarization ratio ρ predicted by MB shows disagreement in the whole frequency range with the experimental results, in which ρ is always much larger than the value calculated by MB and does not show remarkable decrease when $\omega \to \infty$ as predicted by MB.[4] Recently Tao *et al.*[4] tried analysis of boson peak by second-order Raman scattering with the hydrodynamical dipole-induced dipole scattering model (DID).[5] They found good agreement between the observed values of the depolarization of lithium chloride glass and the theoretical value 0.75 which DID predicts. They also explained qualitatively by mode-coupling theory[6] the fact that the boson peak always appears in a liquid-glass transition. Their calculation, however, cannot reproduce the appearance of boson peak above T_g, and this discrepancy prevents quantitative explanation of the temperature dependence. Furthermore the depolarization ratio of MB depends on the type of correlation function used as shown in Sec. IV.

Glycerol is a typical hydrogen-bonded liquid,[7] and it easily undergoes a liquid-glass transition at about 193 K even on slow cooling. Various properties have been studied by dielectric and elastic dispersions, heat capacity spectroscopy, viscosity, etc. The structural properties were also recently investigated in the liquid-glass transition of D-glycerol.[8-10]

In order to clarify the physical meaning of low-frequency spectra, consideration of both line shape and depolarization ratio is very important. Therefore in the present study both VV and VH Raman spectra were carefully measured in glycerol.

II. EXPERIMENT

The sample used was obtained from the Wako Chemical Co. Ltd., with the 99.5% purity. It was sealed in a quartz optical cell with the size 7 mm $\times$ 7 mm $\times$ 12 mm and was kept in the copper block of a conventional cryostat. The temperature of the cell was controlled within ± 0.5 K. The exciting source for the Raman scattering measurements is a 5145 Å light of power 200 mW from an Ar-ion laser. It illuminates the sample through a lens of focal length 200 mm. The scattered light was collected at right-angle scattering geometry by a lens of focal length 100 mm, and was analyzed by an additive-dispersion triple monochromator (Jobin Yvon, T64000) with resolution 2 cm^{-1}. The depolarization ratio was accurately determined by the use of high-quality prism polarizers of extinction ratio 5×10^{-6}. The illuminated region in the sample was always monitored by television at 300 magnification to avoid microbubbles and striae which affect the depolarization ratio. The output signals from the spectrometer were finally detected by the photon counting technique with a photomultiplier (Hamamatsu Photonics, R464S).

III. EXPERIMENTAL RESULTS

Figure 1 shows the temperature variation of the VV polarized Stokes Raman spectra in the temperature range from 90 to 333 K. When the temperature decreases, the width of the Rayleigh wing decreases remarkably at first and then a low-frequency broad response appears below about 270 K. The peak frequency gradually becomes higher above T_g, whereas below T_g the peak position hardly moves and its intensity slightly decreases. The "light scattering excess"[11] which appears between the Rayleigh component and boson peak is very weak below T_g, and it decreases on further cooling. These properties are observed in both VV and VH depolarized spectra.

The depolarization ratio $\rho(\omega) = I_{VH}/I_{VV}$ of glycerol was also determined at temperatures from 90 to 333 K. Typical results are shown in Fig. 2. It is found that $\rho(\omega)$
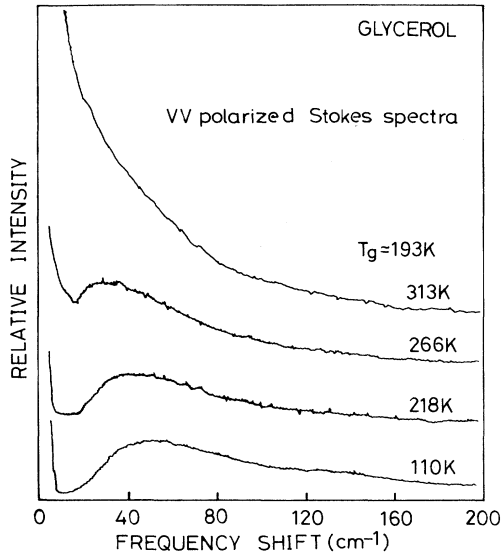
FIG. 1. The temperature dependence of the low-frequency VV polarized Stokes spectra of glycerol.

is nearly constant (~ 0.53) from 5 cm^{-1} to 200 cm^{-1}, and it hardly depends on temperature.

The temperature dependence of the peak frequency is shown in Fig. 3. The presence of the kink near 195 K is indicative of the liquid-glass transition. The temperature variation reflects the change of sound velocity, which also shows the kink at around T_g.[12]

IV. DISCUSSION

A. Line shape of boson peak

The line shape of boson peak was compared with calculations based on both the Gaussian and the exponential correlation functions. According to the MB model, in which the Gaussian correlation function $\exp\{-(r/\sigma)^2\}$ is used, the VV polarized intensity $I_{VV}(\omega)$ is given by

$$\frac{I_{VV}(\omega)}{\omega[n(\omega)+1]} = \{2g_t(\omega)+(15V+\tfrac{2}{3})g_l(\omega)\}\omega^2, \qquad (1)$$

where $n(\omega)$ and V denote the boson factor and the photoelastic term, respectively. The Fourier transform of the structural correlation function of the transverse acoustic mode $g_t(\omega)$ and that of the longitudinal one $g_l(\omega)$ are given by

$$g_t(\omega) = \left[\frac{V_1}{V_t}\right]^5 \exp\left\{-\left[\frac{2\pi\sigma c\omega}{V_t}\right]^2\right\}, \qquad (2a)$$

$$g_l(\omega) = \exp\left\{-\left[\frac{2\pi\sigma c\omega}{V_1}\right]^2\right\}, \qquad (2b)$$

where c, σ denote the light velocity, and the structural correlation length, respectively, and ω is in cm^{-1}. V_t, V_l are the transverse and longitudinal acoustic velocity. When the correlation function is the exponential one $\exp(-r/\sigma)$, $g_t(\omega)$ and $g_l(\omega)$ are replaced by
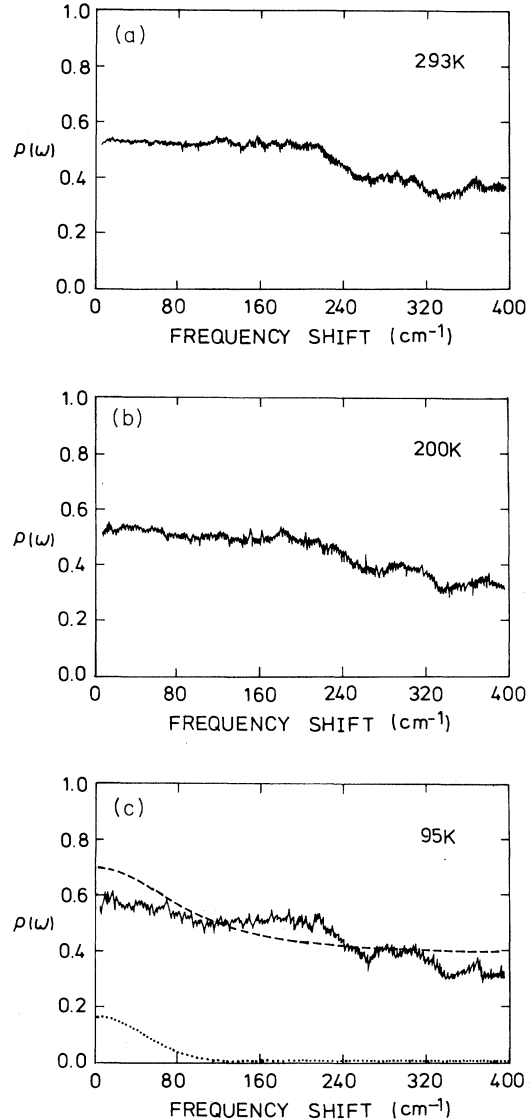

FIG. 2. The depolarization ratio $\rho(\omega)=I_{VH}/I_{VV}$ of glycerol (a) 293 K, (b) 200 K, and (c) 95 K. The dashed and dotted lines show the calculated values by the exponential and the Gaussian structural correlation functions, respectively.

$$g_t(\omega) = \left[\frac{V_l}{V_t}\right]^5 \frac{1}{\{(2\pi\sigma c\omega)^2+(v_t/\sigma)^2\}^2}, \qquad (3a)$$

$$g_l(\omega) = \frac{1}{\{(2\pi\sigma c\omega)^2+(v_l/\sigma)^2\}^2}. \qquad (3b)$$

The line shape was fitted by the two functions at first as shown in Fig. 4, where the values of v_l/v_t and V are assumed to be 1.9 and 12. The structural correlation length is estimated to be about 14 Å and it is almost independent of the temperature. According to a recent neutron experiment, the structural correlation was observed below 20 Å in D-glycerol, for which the glass transition is very similar to that of glycerol.[8,9] The size of a molecule of glycerol is about 5 Å and the structural correlation

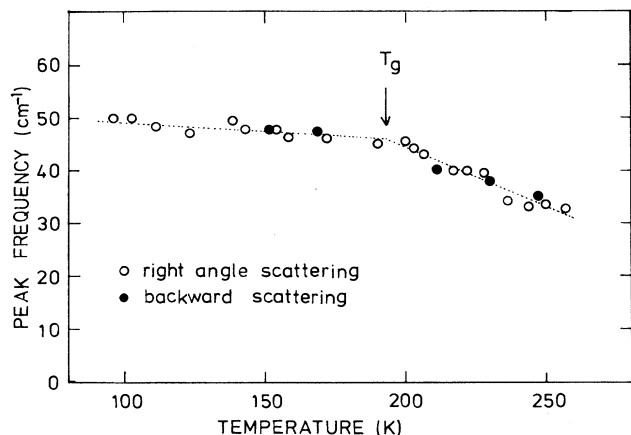FIG. 3. The temperature dependence of the peak frequency of "boson peak" in VV polarized Stokes spectra of glycerol.

FIG. 4. The VV polarized spectra of "boson peak" at 95 K $< T_g$. The dashed and dotted lines show the calculated values by the exponential and the Gaussian structural correlation functions, respectively.

length may be related to the mean size of clusters of hydrogen-bonded molecules in a supercooled state.

B. Low-frequency depolarization ratio

The depolarization ratio was also analyzed using both the Gaussian and the exponential correlation function as shown in Fig. 2(c), where the depolarization ratio $\rho(\omega)$ was calculated by the equation[1]

$$\rho(\omega) = I_{VH}/I_{VV} = \left[\frac{4}{3} + \frac{30V}{2+3g_t/g_l} \right]^{-1}. \qquad (4)$$

The calculated values with the Gaussian type were much lower than the observed values, whereas the values with the exponential one are in agreement with the observed values.

The observed results for glycerol are very similar to those of lithium chloride glass,[4] though Ref. 4 does not give the data for the depolarization ratio below T_g. Their analysis by the mode-coupling theory already succeeded in verifying the existence of both slow and fast relaxation modes in very low-frequency spectra (below 1 cm^{-1}).[13] With regard to the low-frequency Raman spectra, however, it is not clear why the second-order scattering due to DID is much stronger than the disorder-induced scattering of the MB model. The major drawback of the MB model, the discrepancy of the depolarization ratio between the observed values and those predicted by the MB model, can be removed by the appropriate choice of correlation function as described above.

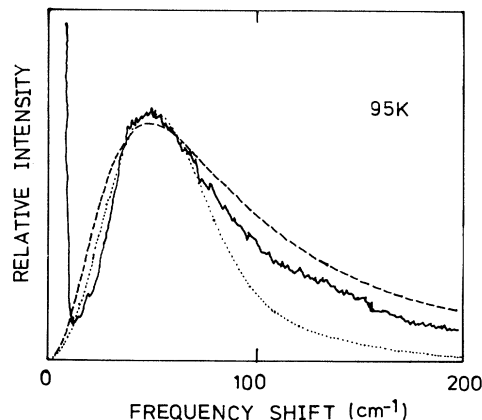In order to clarify the origin of boson peak of the glycerol, more work is still needed. With information from inelastic neutron scattering technique, which gives the one-phonon vibrational density of states, a coherent picture of boson peak may emerge.

V. CONCLUSION

(1) When the temperature decreases, boson peak always appears far above T_g in both VV and VH spectra. The peak frequency of boson peak hardly depends on temperature below T_g.

(2) The low-frequency depolarization ratio hardly depends on temperature from 90 to 333 K.

(3) The discrepancy of the depolarization ratio of boson peak between the observed data and the values predicted by the MB model is partly removed by the calculations based on the exponential correlation function.

(4) The structural correlation length is estimated to be 14 Å. It may be related to the mean size of the hydrogen-bonded clusters of molecules.

ACKNOWLEDGMENTS

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