

Low-frequency Raman scattering by defects in glasses

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(Received 16 September 1975)

We describe the excess Raman intensity recently observed by Winterling in vitreous silica for frequency shifts $\omega < 20 \text{ cm}^{-1}$ in terms of structural relaxation of defects, which can have two distinct states of polarizability differing by an amount $\Delta\alpha = 0.6 \text{ \AA}^3$. All other properties of the defects (distribution of potential barriers) are taken from ultrasonic data. The correct temperature dependence is obtained. The experimentally observed value for the depolarization ratio in vitreous silica (0.30 ± 0.03) can be explained if the simplest possible form of the polarizability difference between the two states is assumed. We briefly discuss Raman scattering by quantum-mechanical tunneling states, which should be observable at very low temperatures.

I. INTRODUCTION

The low-temperature properties of glasses have been widely investigated in recent years. Measurements of the specific heat¹ suggest the existence of excitations other than phonons. According to Anderson, Halperin, and Varma² and Phillips³ these defects (represented by a double-well potential) may be approximated by two-level systems. Studies of the ultrasonic attenuation as a function of temperature (at frequencies around 100 MHz) suggest a two-peak structure. The low-temperature peak ($\sim 4 \text{ K}$) can be traced back⁴ to two-level systems relaxing via quantum-mechanical phonon-assisted tunneling.⁵ The high-temperature ($\sim 50 \text{ K}$) peak⁶ can also be interpreted in terms of structural relaxation of defects of a more general nature; in this case relaxation occurs via thermal activation.^{4,7}

Light-scattering experiments provide us with information about both static and dynamic properties of glasses. Thus, the breakdown of translational invariance gives rise to "disorder-induced scattering,"⁸⁻¹⁰ i. e., scattering from all normal modes of a given frequency—essentially an effect of static disorder. Furthermore, low-frequency ($\omega < 20 \text{ cm}^{-1}$) Raman scattering¹¹ has revealed an intensity which is in excess of that expected from disorder-induced scattering by Debye phonons. In what follows, we show that this can be the result of incoherent scattering by defects relaxing via thermal activation. These are the same defects which cause the high-temperature peak in the ultrasonic attenuation. This typical "Rayleigh-wing" structure is formally identical to the one obtained from fluctuations in the orientation of anisotropically polarizable molecules in a liquid.¹² The physical difference is that here we do not deal with reorientation, but rather with "hopping" between two distinct states of an otherwise rigid defect whose polarizabilities differ by an amount $\Delta\alpha$.

The paper is divided into three parts. Section

II gives a brief account of scattering due to the (static) disorder. Section III deals with the main topic—scattering by structurally relaxing defects. Finally, in Sec. IV we discuss scattering by quantum-mechanical tunneling states.

II. STATIC DISORDER

The most obvious difference regarding light scattering from amorphous solids as compared to crystals comes from the breakdown of translational invariance. Martin and Brenig¹⁰ distinguish two types of disorder: (i) electrical disorder,⁸ as expressed by short-range fluctuations of elasto-optical constants, and (ii) a particular form of mechanical disorder, which involves the "distortion" of plane waves but not their damping. We can see that (iii) damping mechanisms can also lead to a violation of the momentum selection rule (and hence may become important for Raman scattering) if we consider a phonon with wave vector q_j and mean free path Λ_j , for which $q_j\Lambda_j \lesssim 1$. Thermal conductivity data,¹ however, indicate that this overdamping condition is not fulfilled for phonons in the low-frequency region $\omega < 35 \text{ cm}^{-1}$. Shuker and Gammon⁹ have also expressed the idea that the momentum selection rule may be violated as a result of strong spatial decay of the phonon modes. However, their criterion differs from ours (iii) since it involves the optical rather than the phonon wavelength.

Now it turns out that (i) and (ii) contribute similar terms, in additive fashion, to the expressions for the scattered intensities,¹⁰ whereas damping mechanisms (iii) are as we mentioned above unimportant in the low-frequency region. Therefore, we may formally combine (i) and (ii) and formulate the theory in terms of electrical disorder alone. Light scattering is then caused by time-dependent fluctuations of the electrical susceptibility $\delta\chi_i$, which, in turn, originate in the local strains e_j :

$$\delta\chi_i(\vec{r}, t) = -(\epsilon^2/4\pi) [p_{ij} + \delta p_{ij}(\vec{r})] e_j(\vec{r}, t). \quad (1)$$

The Voigt notation has been used in (1), ϵ is the dielectric constant, p_{ij} represent macroscopic averages of elasto-optical (Pockels) constants, and $\delta p_{ij}(\mathbf{r})$ represent their local (static) fluctuations.

The spectral intensity of the scattered light is given in terms of the quantities

$$I_{ij}(q, \omega) = I_0 \left(\frac{\omega_0}{c} \right)^4 \int d\vec{r} dt e^{i\vec{q} \cdot \vec{r} - i\omega t} \\ \times \langle \delta \chi_i(\vec{r}, t) \delta \chi_j(0, 0) \rangle,$$

where ω_0 and I_0 are, respectively, the frequency and intensity of the incident light, and \vec{q}, ω represent the wave vector and frequency difference between incident and scattered light. In a 90°-geometry scattering experiment the polarized and depolarized components of the spectrum are given, respectively, by $I_{\perp\perp} = I_{11}$ and $I_{\perp\parallel} = I_{44}$. The indices \perp, \parallel (or \perp, \parallel) denote the polarization of incident and scattered light relative to the scattering plane. If we restrict ourselves to electrical disorder and assume an isotropic Debye spectrum for undistorted plane-wave phonons, we obtain for the low-frequency polarized Stokes component a spectral intensity

$$\frac{I_{\perp\perp}^{\text{dis}}(\omega)}{\omega[n(\omega)+1]} = I_0 \left(\frac{\epsilon \omega_0}{c} \right)^4 \frac{\lambda(0) C_t^2 \omega^2}{64 \pi^4 \rho v_t^5} \\ \times \left[1 + \frac{4}{45} \left(\frac{C_t}{C_l} \right)^2 + \frac{2}{15} \left(\frac{v_l}{v_t} \right)^5 \left(\frac{C_t}{C_l} \right)^2 \right]. \quad (2)$$

Here, v_l and v_t are the longitudinal and transverse sound velocities, $3C_l = p_{11} + 2p_{12}$, $C_t = p_{11} - p_{12}$, ρ is the density of the medium, and $n(\omega) = 1/(e^{\beta\hbar\omega} - 1)$ is the phonon occupation number. The factor ω^2 reflects the acoustic phonon density of states, which includes both longitudinal and transverse phonons. Finally, $\lambda(0)$ is the long-wavelength limit of the correlation function $\lambda(\vec{k}) = \int d^3r e^{-i\vec{k} \cdot \vec{r}} \langle \delta p_{ij}(\vec{r}) \delta p_{kl}(0) \rangle / p_{ij} p_{kl}$ of the static fluctuations of the elasto-optical constants. In terms of $\lambda(0)$, the mean square fluctuations of p_{ij} , averaged over a macroscopic volume Ω , are given by $\langle (\delta p_{ij}/p_{ij})^2 \rangle_\Omega = \lambda(0)/\Omega$. The condition $\lambda(\omega/v_t) \cong \lambda(0)$, which means that the acoustic phonon wavelength must be larger than the correlation length of electrical disorder, limits the validity of Eq. (2) to low frequencies. If we assume that essentially all the Raman intensity at $\omega = 20 \text{ cm}^{-1}$ is electrical disorder induced, we obtain from the data of Winterling¹¹ and Eq. (2) a value of $\lambda(0) = 1400 \text{ \AA}^3$ for vitreous silica. On the basis of "frozen-in" density fluctuations¹³ $\delta \rho(\vec{r})$, we would obtain $\delta p_{ij}(\vec{r}) = (\gamma/\rho) p_{ij} \delta \rho(\vec{r})$, and thus

$$\lambda(0) = (\gamma/\rho)^2 \int d^3r \langle \delta \rho(\vec{r}) \delta \rho(0) \rangle \\ \lesssim \gamma^2 k_B T_g \kappa_T(T_g) = 0.4 \text{ \AA}^3,$$

which is several orders of magnitude smaller than

the value derived from experiment. Here $\gamma = \partial \ln p_{ij} / \partial \ln \rho$ is a Gruneisen parameter for the elasto-optical constants which is of order unity¹⁴ and $\kappa_T(T_g) = 2.1 \times 10^{-12} \text{ dyn}^{-1} \text{ cm}^2$ is the isothermal compressibility at the glass transition temperature T_g .¹⁵ This discrepancy suggests either that "frozen-in" anisotropy fluctuations—similar to those occurring in liquids—might be of much greater importance in determining electrical disorder than the density fluctuations, or that in fact mechanical disorder (ii) rather than electrical disorder is the main cause of disorder-induced scattering.

An expression similar to (2) can be obtained for the depolarized intensity $I_{\perp\parallel}$. Substituting the elastic and elasto-optical constants of fused quartz, one obtains a depolarization ratio $I_{\perp\parallel}/I_{\perp\perp} = 0.28$.

III. STRUCTURAL RELAXATION OF DEFECTS

In what follows, we explain the excess scattering intensity found by Winterling at low-frequency shifts ($\omega < 20 \text{ cm}^{-1}$) by the coupling of light to localized structural defects with two configuration states. The ultrasonic and microwave absorption peaks occurring between 50 and 300 K have been successfully interpreted in terms of the relaxation of such defects.⁷ The main point of the present paper is to relate the recent Raman data to these older ultrasonic and microwave data. We describe the state of each defect by a pseudospin variable S_j^z which can have the value $+\frac{1}{2}$ or $-\frac{1}{2}$. Our basic assumption is that the two-defect states are states of different electric polarizability. The time-dependent part of the electric polarizability tensor of the j th defect is determined by the instantaneous value of the pseudospin variable and by the polarizability difference between the two possible defect states. Brought into diagonal form, it can be written

$$\begin{pmatrix} \Delta \alpha_j^{(1)} & 0 & 0 \\ 0 & \Delta \alpha_j^{(2)} & 0 \\ 0 & 0 & \Delta \alpha_j^{(3)} \end{pmatrix}. \quad (3)$$

Every tensor component is time dependent according to

$$\Delta \alpha_j^{(i)}(t) = \Delta \alpha_j^{(i)} S_j^z(t),$$

where $S_j^z(t)$ can take the discrete values $\pm \frac{1}{2}$ of $-\frac{1}{2}$, corresponding to the defect's instantaneous state.

In the simplest case only one component of the tensor (3) is nonzero: $\Delta \alpha_j^{(1)} = \Delta \alpha_j^{(2)} = 0$, $\Delta \alpha_j^{(3)} \equiv \Delta \alpha_j \neq 0$. Our subsequent calculation is made for this case. Compared with the case of anisotropic molecules in a liquid, which give rise to a Rayleigh wing through their rotational motion, the situation here is different, since the motion of a two-state defect in a glass is limited to the hopping between

the two configurational states with spatially fixed polarizabilities. The spatial orientation of different defects in the glass, however, is random as for molecules in a liquid.

The dynamics of the two-state defects which enters the scattering cross section is expressed in terms of the time-dependent polarizability auto-correlations:

$$\begin{aligned} & \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \Delta\alpha_j(t) \Delta\alpha_j(0) \rangle \\ &= (\Delta\alpha_j)^2 \int_{-\infty}^{\infty} dt e^{i\omega t} \langle S_j^x(t) S_j^x(0) \rangle \\ &= (\Delta\alpha_j)^2 \frac{\chi_{j,x}''(\omega)}{1 - e^{-\beta\hbar\omega}}. \end{aligned} \quad (4)$$

The third line in Eq. (4) is derived using the fluctuation-dissipation theorem. $\chi_{j,x}''(\omega)$ is the imaginary part of the longitudinal pseudospin susceptibility $\chi_{j,x}(\omega)$ discussed in the context of sound attenuation⁴; for defects which can relax via thermal activation

$$\chi_{j,x}(\omega) = \frac{\beta}{4} \frac{1}{1 - i\omega\tau_j}, \quad (5)$$

where $\tau_j^{-1} = \tau_0^{-1} e^{-\beta V_j}$ is the rate of thermally activated transitions for a potential barrier of height V_j . We employ the broad Gaussian distribution of barrier heights $P(V) = \bar{P} \exp[-(V - V_m)^2/V_0^2]$, where $V_m = 550$ K, $V_0 = 410$ K, $\bar{P} = 5.6 \times 10^{17} \text{ K}^{-1} \text{ cm}^{-3}$ and $\tau_0 = 2 \times 10^{-13}$ sec. These constants are all derived from ultrasonic data in Ref. 7.¹⁶ In the simplest case, where only one component of the polarizability tensor Eq. (3) is nonzero ($\Delta\alpha^{(3)} = \Delta\alpha \neq 0$, $\Delta\alpha^{(1)} = \Delta\alpha^{(2)} = 0$), we obtain for the polarized Raman intensity

$$\begin{aligned} \frac{I^{\text{pol}}(\omega)}{\omega[n(\omega)+1]} &= I_0 \left(\frac{\omega_0}{c} \right)^4 \left(\frac{\epsilon+2}{3} \right)^2 \frac{3}{15} (\Delta\alpha)^2 \\ &\times \frac{1}{2\pi} \frac{\beta}{4} \int dV P(V) \frac{\tau(V)}{1 + \omega^2 \tau^2(V)}, \end{aligned} \quad (6)$$

where $(\Delta\alpha)^2$ is some average over all $(\Delta\alpha_j)^2$, and the factor $\frac{3}{15}$ comes from the angular averaging over the random defect orientations. We have also taken account of the fact that the effective electric field at each defect is in fact $\frac{1}{3}(\epsilon+2)$ times the applied field. The result Eq. (6) demonstrates explicitly the relationship between the Raman scattering intensity and the ultrasonic attenuation. The right-hand side of Eq. (6) is proportional to $I_{\text{re1}}^{-1}(\omega)/\omega^2$, where $I_{\text{re1}}^{-1}(\omega)$ is the inverse mean free path of phonons of frequency $\omega/2\pi$ which arises from the defect relaxation.

The depolarized intensity I_{\perp} can be obtained in an identical fashion, the only difference being that the angular average now yields a factor $\frac{1}{15}$. Thus, a depolarization ratio $I_{\perp}/I_{\parallel} = \frac{1}{3}$ is obtained. In the

general case, when more than one components of the polarizability tensor (3) are nonzero, the depolarization ratio is given by¹⁷

$$\frac{I_{\perp}}{I_{\parallel}} = \frac{1}{2} \frac{\gamma - 1}{1 + \frac{2}{3}\gamma},$$

where

$$\gamma = 3 \sum_{i=1}^3 (\Delta\alpha^{(i)})^2 / \left(\sum_{i=1}^3 \Delta\alpha^{(i)} \right)^2.$$

Since γ ranges from 1 to ∞ , the range of the depolarization factor is between zero and $\frac{3}{4}$. Since defects with the same structure should have the same form of polarizability difference Eq. (3), the depolarization ratio may be considered as a structural characteristic of the defects. The experimental value for fused silica¹¹ is 0.30 ± 0.03 , which is, within the experimental uncertainty, equal to the value obtained for only one polarizability component ($\frac{1}{3}$). Winterling has very recently extended his Raman measurements to other glasses¹⁸ and found for B_2O_3 glass a depolarization factor of 0.47. This result indicates that the structure of the defect states is different in B_2O_3 glass and in vitreous silica, which is not too surprising, considering the different basic structural units of the two glasses, planar BO_3 triangles vs SiO_4 tetrahedra.

Our predicted temperature dependence of the Raman intensity is shown in Fig. 1 for a frequency shift of 5 cm^{-1} . The calculated solid curve has the form of the ultrasonic attenuation curves at high

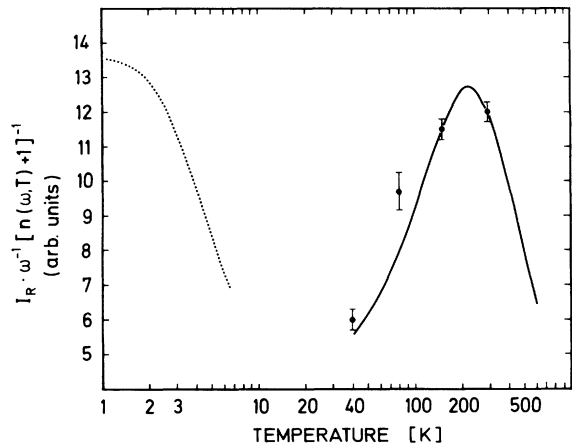


FIG. 1. Reduced Raman intensity $I_R \omega^{-1} [n(\omega) + 1]^{-1}$ vs temperature T for a given frequency shift ($\omega = 5 \text{ cm}^{-1}$). The solid curve includes contributions from disorder-induced scattering [Eq. (2)] and from structural relaxation of anisotropically polarizable defects [Eq. (6)]. The contribution of the disorder-induced scattering has a constant value which in these units is equal to 1.06, less than 10% of the total intensity observed at room temperature. The dotted curve represents scattering by direct Raman processes [Eq. (7)].

frequencies¹⁹ since ultrasonic data have been used to determine the distribution $P(V)$ of barrier heights. In the measured temperature range, satisfactory agreement for the temperature dependence is obtained. For higher temperatures our calculation predicts a decrease of the reduced intensity²⁰ $I\omega^{-1}(n+1)^{-1}$.

To obtain agreement with the experiment, a value of $\Delta\alpha = 0.6 \text{ \AA}^3$ is required, i.e., $\Delta\alpha_j(t) = \pm 0.3 \text{ \AA}^3$ according to whether $S_j^z = \pm \frac{1}{2}$. This is a reasonable value compared with the empirically fitted, effectively isotropic polarizability of O^{2-} in SiO_2 (1.7 \AA^3).²¹

In his paper, Winterling¹¹ discusses as a second possibility the explanation of his data in terms of low-frequency "tails" of damped high-frequency phonons ($120 > \omega_q > 20 \text{ cm}^{-1}$). In this case the light couples to the elastic strain field [see Eq. (1)] which is described by the phonon propagator $D(q, \omega)$ as used in Ref. 22. If the assumption is made that the low-frequency tails of the phonons are due to the relaxation of structural two-state defects,⁴ this contribution can be ascribed to an "indirect coupling" of light to such defects via the elastic strain field. However, the result for the light scattering due to this "indirect coupling" is formally identical to the result of the "direct coupling" discussed before, since the low-frequency portion of the short-wavelength phonon propagator $D(q, \omega)$ is (for $\omega \ll \omega_q$) just proportional to $\chi_z(\omega)$, the longitudinal pseudospin susceptibility [Eq. (5)]. The obvious interpretation of this result is that the low-frequency tails of the phonon propagator describe the fluctuations of the elastic strain field in the vicinity of every defect, which follow the hopping of the defect between its two states. The strain field around a defect can be considered as an "elastic polarization." According to this interpretation, the contribution to the light scattering of the "indirect coupling" comes from the fluctuating "elastic polarization" around the defects. Since it may be difficult to distinguish between "defect center" and "polarization cloud," and also since only one coupling constant can be determined from a fit of the experimental data, it is reasonable to consider the contributions of the "elastic polarization" and the "defect center" as combined into an effective electric polarizability $\Delta\alpha_j$ of the total defect. With such a value of $\Delta\alpha$ our results Eq. (6) include the effect of both "direct" and "indirect" coupling.

IV. QUANTUM-MECHANICAL TUNNELING STATES

In order to ascertain the role of two-state defects in light scattering one should look for the analog of the resonant processes which were detected in ultrasonic experiments at very low temperatures. This consists of the absorption and reemission of

a light quantum by a defect, whereby the defect jumps from one quantum-mechanical state to the other. In order to describe such a process, the polarizability anisotropy $\Delta\alpha_j(t)$ must be considered as an operator; within the pseudospin formalism this corresponds to an ansatz of the type

$$\Delta\alpha_j(t) = \sum_{\mu=1}^3 \Delta\alpha_j^{\mu} S_j^{\mu}(t).$$

If $\Delta\alpha_j^{\mu}$ is roughly independent of μ (as is the case with the analogous deformation Hamiltonian⁴) we obtain

$$\frac{I_{11}^{\text{tun}}(\omega)}{\omega[n(\omega)+1]} = I_0 \left(\frac{\omega_0}{c}\right)^4 \left(\frac{\epsilon+2}{3}\right)^2 \times \frac{3}{15} (\Delta\alpha)^2 (1/4\omega) N(\omega) \tanh\left(\frac{1}{2}\beta\omega\right), \quad (7)$$

where $N(\omega)$ is the density of states of the two-state defects.

Using the constant density of states $N = 7.2 \times 10^{32} \text{ erg}^{-1} \text{ cm}^{-3}$ derived from specific-heat data¹ and the same $\Delta\alpha = 0.6 \text{ \AA}^3$ as in Eq. (6), we obtain the dotted curve in Fig. 1 for the Raman intensity as a function of temperature at a frequency shift $\omega = 5 \text{ cm}^{-1}$. Note that: (i) For $T \lesssim 3 \text{ K}$, I_{11}^{tun} is of the same order of magnitude as I_{11}^{rel} ($T = 40 \text{ K}$). Thus, coupling to the quantum-mechanical defects should be detectable. (ii) Relaxational contributions due to phonon-assisted tunneling are not considered; these only become important for $T > 10 \text{ K}$, at which temperatures quantum-mechanical two-level systems cease to give a good description of the defects.⁴ (iii) This Raman scattering by directly induced transitions is less likely to be saturated than the resonant ultrasonic attenuation, since the scattering rate is proportional to $[1 - f(\omega)]$, in contrast to the ultrasonic absorption rate which is proportional to $[\frac{1}{2} - f(\omega)]$, where $f(\omega)$ is the occupation number of the excited defect state.

V. CONCLUSIONS

We have shown that the excess Raman intensity observed in silica for intermediate temperatures ($40 < T < 300 \text{ K}$) can be interpreted in terms of scattering from structurally relaxing two-state defects—the same defects which are responsible for ultrasonic attenuation in the 1-GHz range. Two additional features of our results can be subjected to experimental test: the decrease in reduced intensity predicted for higher temperatures ($600 > T > 300 \text{ K}$) and the increase that should occur for very low temperatures ($T \lesssim 3 \text{ K}$) due to scattering from quantum-mechanical two-level systems.

The proportionality of Raman scattering intensity and sound attenuation, which is the main point of this paper, would be most clearly demonstrated if Raman experiments were performed in the ultrasonic frequency range. This would require using

very high resolution spectroscopy in the range $0.1\text{--}0.001\text{ cm}^{-1}$. If our theoretical predictions are verified, we would have a unified description of ultrasonic, microwave, and Raman data on glasses in terms of the same structural two-state defects.

We wish to thank Dr. G. Winterling for informing us about recent measurements and for helpful discussions. Comments from Dr. A. Martin, Dr. S. Hunklinger, and Professor R. Klein are also acknowledged.

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- ¹R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971); R. B. Stephens, Phys. Rev. B **8**, 2896 (1973).
²P. W. Anderson, B. I. Halperin, and C. Varma, Philos. Mag. **25**, 1 (1972).
³W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).
⁴J. Jäckle, L. Piché, W. Arnold, and S. Hunklinger, J. Non-Cryst. Solids (to be published).
⁵J. Jäckle, Z. Phys. **257**, 212 (1972).
⁶O. L. Anderson and H. E. Bömmel, J. Am. Ceram. Soc. **38**, 125 (1955).
⁷S. Hunklinger, in *Proceedings of the Satellite Symposium on Microwave Acoustics of the Eighth International Congress on Acoustics*, edited by E. R. Dobbs and J. K. Wigmore (Lancaster, 1974), and references cited therein.
⁸E. Whalley and J. E. Bertie, J. Chem. Phys. **46**, 1264 (1967).
⁹R. Shuker and R. W. Gammon, Phys. Rev. Lett., **25**, 222 (1970).
¹⁰A. Martin and W. Brenig, Phys. Status Solidi B **64**, 163 (1974).
¹¹G. Winterling, Phys. Rev. B **12**, 2432 (1975).
¹²R. D. Mountain, Crit. Rev. Solid State Sci., **1**, 5 (1970).
¹³N. L. Laberge, V. V. Vasilescu, C. F. Montrose, and P. B. Macedo, J. Am. Ceram. Soc. **56**, 506 (1973).
¹⁴H. E. Shull and K. Vedam, J. Appl. Phys. **43**, 3724 (1972).
¹⁵R. W. Douglas and J. O. Isard, J. Soc. Glass Technol. **35**, T206 (1951).
¹⁶In contrast to Ref. 7 we do not impose a cutoff on low potential-energy barriers.
¹⁷I. L. Fabelinskii, *Molecular Scattering of Light* (Plenum, New York, 1968), Chap. I.4.
¹⁸G. Winterling, in *Proceedings of the Third International Conference on Light Scattering in Solids*, Campinas, 1975 (unpublished).
¹⁹(a) A. S. Pine, Phys. Rev. **185**, 1187 (1969); (b) J. R. Sandercock (unpublished).
²⁰Preliminary measurements by Winterling show a very small decrease in the reduced intensity as the temperature increases. An analogous "broadening" of the intensity maximum occurs in ultrasonic attenuation (Brillouin linewidth vs T , Ref. 19(b) for higher frequencies ($\omega \sim 35\text{ GHz}$); these observations indicate that defects with high potential barriers, hitherto suppressed because of the particular form of the distribution $P(V)$, may in fact become relevant.
²¹J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).
²²P. Fulde and H. Wagner, Phys. Rev. Lett. **27**, 1280 (1971).