Spectroscopic Observation of Very-Low-Energy Excitations in Glasses

P. A. Fleury and K. B. Lyons
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 20 January 1976)

The frequency spectra of anomalous very-low-energy excitations (0–0.3 cm^{-1}) in glasses have been measured by inelastic light scattering for a variety of compositions and temperatures. Possible sources for these spectra include configurational degrees of freedom associated with the low-temperature tunneling states.

The anomalous and apparently universal low-temperature thermodynamic,[1] transport,[2] and acoustic[3] properties of glasses are thought to arise from tunneling[4] among very-low-energy states. In this paper we report the direct observation by inelastic light scattering of an anomalous very-low-frequency feature in several metal-oxide glasses. The scattering strength, polarization selection rules, and linewidths (< 10 GHz) of this feature have been determined for temperatures ranging between 60 and 400°K. Several silica, germania, and borosilicate glasses also examined do not exhibit this anomalous "central peak," indicating either the absence of such low-energy excitations or (more likely) their small polarizabilities in these glasses.

The major experimental problem to be overcome in such quasielastic-light-scattering experiments is the very large elastic scattering due to static refractive-index inhomogeneities which in the more complex glasses is four or five orders of magnitude stronger than the inelastic scattering from phonons or other excitations. The use of molecular iodine vapor as a resonant reabsorber[5] together with a conventional grating spectrometer permitted the first indication of a nonelastic low-frequency feature in the Schott LaSF-7 glass recently by Firstein, Cherlow, and Hellworth.[6] However, those experiments were of insufficient resolution to permit extraction of linewidth or spectral-shape characteristics of the central peak.

Our experimental system consists of a stabilized single-frequency 5145-Å argon laser and a temperature-controlled (±0.01°C) I_2 cell. The significant improvements lie in (1) the use of a tandem pressure-scanned Fabry-Perot interferometer (FP) and (2) computer-assisted numerical normalization procedures.[7] The tandem FP has a transmission peak width of ~0.06 cm^{-1} full width at half-maximum (FWHM) and a periodic repeat distance of ~23 cm^{-1}. The complete instrumental response function $N(\nu)$ (i.e., tandem FP plus I_2 cell and associated collection optics) is generated by dividing a known spectrum (e.g., depolarized Rayleigh wing scattering from chlorobenzene) taken without the I_2 cell, by the same spectrum taken with the I_2 cell. Figure 1(a) displays $N(\nu)$ for a typical set of experimental conditions over the frequency range of interest. The rich structure requires precise frequency registration of data spectra in order to permit proper quantitative normalization of data.

In Fig. 1(b) is shown the raw data from LaSF-7 glass at right-angle scattering in the polarized (VV) geometry at 175°K. Division of this data by

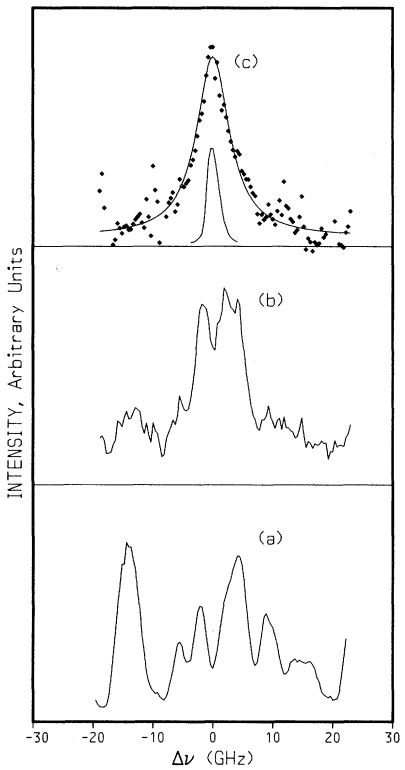

FIG. 1. (a) Complete instrumental response function, $N(\nu)$, centered at the single-mode argon-ion laser frequency (5145-Å line). (b) Raw data for polarized quasielastic scattering from Schott LaSF-7 glass at 175°K. Scattering angle, 90°. Notch at $\Delta\nu = 0$ is clearly evident. (c) Normalized spectrum of Schott LaSF-7 glass.

the $N(\nu)$ of Fig. 1(a) produces the reconstituted or "normalized" spectrum shown in Fig. 1(c). Note that the structure in the raw data associated with the I_2 absorption structure is properly removed. The fit of the normalized data by a Lorentzian is indicated by the solid line in Fig. 1(c). Also indicated is the instrumental line shape. In all spectra the I_2 cell temperature was adjusted so as to permit a negligible transmission (less than a few percent of the central peak intensity) of the strictly elastic scattered light, when the laser was tuned to resonance.

Several glasses of various compositions were examined at room temperature. Fused silica, and several germania borosilicate glasses as well as Schott SF-7 and SF-9 revealed no detectable dynamic central peak. We have, however, observed central peaks in two other glasses (besides LaSF-7) of significantly different compositions, generously provided by Borrelli of the Corning Laboratory.[8] The first is 65.8 Nb_2O_5, 15.4 Na_2O, 18.8 SiO_2 (numbers indicate weight percent) and will be referred to as 66Nb. The second is 13.5 Nb_2O_5, 11 Ta_2O_5, 32 ThO_2, 15.4 B_2O_3, 19 La_2O_3, 4.5 ZnO in composition and will be referred to as Nb-Ta. This glass has several components in common with the LaSF-7, which consists of mainly B_2O_3, La_2O_3, and ThO_2 with Ta_2O_5 and Nb_2O_5 at the few percent level. Their room-temperature Raman spectra (10–1000 cm^{-1}) are very similar in strength and shape.

At 300°K the two Corning glasses exhibited central peaks of comparable width and intensity to that in LaSF-7. The central-peak integrated intensities observed were (10–20)% as strong as for the longitudinal Brillouin components. For comparison, the Brillouin scattering efficiencies in LaSF-7 and Nb-Ta are about equal to half those in fused silica and 66Nb. The central peak observed here is partly depolarized. For LaSF-7 the depolarization ratio $(I_{HV}+I_{HH})/I_{VV}$ is 0.8 ± 0.2. Here the subscripts refer to the polarization of the incident and scattered light with respect to the scattering (H) plane. For Nb-Ta and 66Nb the values are 0.8 ± 0.3 and 0.6 ± 0.2, respectively. By contrast, for the longitudinal Brillouin components I_{VH}/I_{VV} is $< 10^{-2}$. We note that the central-peak intensity is essentially the same for HV and HH scattering, although for an isotropic material no Brillouin intensity from either the TA or the LA modes is expected or observed in the HH geometry.

In all three glasses the scattered intensity decreased strongly with decreasing temperature,

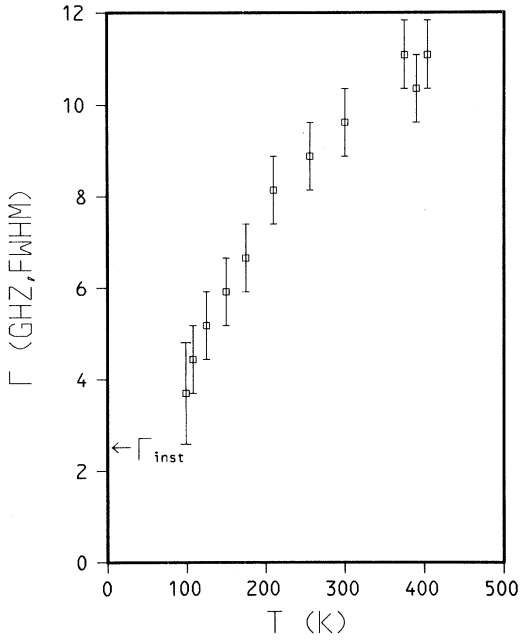

FIG. 2. Temperature dependence of total full width at half-maximum for best-fit Lorentzian to normalized spectra in LaSF-7.

so that no central peak could be observed above the noise for temperatures below ~50°K. Figure 2 shows the total Lorentzian width (FWHM) versus temperature for the LaSF-7 glass. Within experimental error the behavior is well described by $(\Gamma-\Gamma_{inst})=\Gamma_0\exp(-\Delta E/kT)$, where $\Gamma_0=15$ GHz and $\Delta E/k=200$°K. By contrast, over the same temperature range both the Nb-Ta and the 66Nb linewidths are consistent with temperature-independent behavior. The appropriate values of $(\Gamma-\Gamma_{inst})$ are 7.2 ± 1 and 5.5 ± 1 GHz, respectively.

Among the possible mechanisms for the dynamic central peak that we have considered are (1) Rayleigh scattering from entropy fluctuations, (2) scattering from crystal-field electronic levels of rare-earth or transition-metal ions, (3) relaxational contributions to the acoustic-phonon self-energies, and (4) scattering from (a Raman-active subset of) the states responsible for the anomalous thermal properties of glasses below ~1°K.

Rayleigh scattering should produce a fully polarized central peak of much too small a width and intensity to fit our observations. In favor of mechanism (2), the central-peak intensity is observed to increase with rare-earth content,[9] and fluorescence experiments have revealed quite narrow, low-temperature, homogeneous line-

widths for Eu^{3+} in glassy hosts.[10] However, at room temperature these linewidths are much larger ($> 10\times$) than we observe, and our spectra are quite similar for glasses containing ions of widely differing electronic structures. Therefore this mechanism is at best a questionable candidate to account for our observations.

In mechanism (3) a phonon self-energy of the relaxation form $\Sigma = i\omega\delta/(1 - i\omega\tau)$ can introduce into the Brillouin spectrum an additional central component whose width and strength varies with the relative parameter values $(\delta, \tau^{-1}, \omega)$ involved.[11] Such a central peak will have the same polarization selection rules as the phonon (LA or TA) with which the relaxation process is associated. Our polarization observations are thus inconsistent with a relaxation associated solely with *either* longitudinal *or* transverse phonons. However earlier temperature-dependent ultrasonic experiments[12] indicate similar relaxation effects for both longitudinal and transverse modes in several oxide glasses, with relaxation times ranging between 10^{-8}–10^{-11} sec. Thus the central-peak widths we observed may measure the characteristic times for structural or configurational relaxations in our glasses. Our measured central-peak intensity and linewidth would then predict a velocity dispersion of a few percent between low and high (relative to τ^{-1}) frequencies for both longitudinal and transverse sound. Ultrasonic experiments might thus provide a definitive answer as to whether mechanism (3) is an important contribution to the spectral central peaks. We should point out that our observations in the *HH* polarization geometry, where no phonon scattering is allowed, argues against this mechanism being the sole cause of the anomalous spectrum.

Finally, we consider the possibility of light scattering directly from the low-frequency configurational degrees of freedom, which give rise to the tunneling states dominating thermodynamic and transport properties below ~1°K. Acoustic and thermodynamic measurements require that their energies span a frequency range of at least 1 cm^{-1}, somewhat larger than the maximum extent (~0.3 cm^{-1}) of our spectral peak. Further, the tunneling states exist even in those glasses, like SiO_2, in which we have observed no central peak. These discrepancies might be attributed to differences in the ways that photons and phonons couple to the configurational degrees of freedom. Light scattering is sensitive only to the Raman-active subset of these. And the strength of Raman activity is expected to depend on the glass composition more sensitively than do the acoustic or thermodynamic properties.[13] The fact that the glasses displaying the central peak are composed of heavy-metal oxides, whereas those which do not are oxides of B, Si, and Ge, is consistent with this viewpoint. The larger scattering cross sections in the multicomponent glasses may also be due in part to enhancements by local strains expected to be larger in the more complex glass compositions.

As the foregoing speculations on mechanisms suggest, considerably more experimental and theoretical work is required—particularly as functions of controlled glass composition, etc.—before the nature of these new excitations is understood. Nonetheless the present experiments reveal the important and previously lacking *frequency spectrum* of the very-low-energy Raman-active excitations in glasses.

We are grateful to N. F. Borrelli and A. D. Pearson for samples and helpful discussions, to R. W. Hellwarth for open discussion of Ref. 6 prior to publication and for suggesting we investigate the Borrelli glasses, to B. Golding and C. M. Varma for useful comments on the manuscript, and to H. L. Carter for able technical assistance.

[1]R. C. Zeller and R. O. Pohl, Phys. Rev. B 4, 2029 (1971).

[2]R. B. Stephens, Phys. Rev. B 8, 2896 (1973); J. C. Lasjaunias, D. Thoulouze, and F. Pernot, Solid State Commun. 14, 957 (1974).

[3]B. Golding, J. E. Graebner, B. I. Halperin, and R. J. Schutz, Phys. Rev. Lett. 30, 223, 1973; S. Hunklinger, W. Arnold, S. Stein, R. Nava, and K. Dransfeld, Phys. Lett. 42A, 253 (1972), and 45A, 311 (1973).

[4]P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1972); W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).

[5]G. E. Devlin, J. L. Davis, L. Chase, and S. Geschwind, Appl. Phys. Lett. 19, 138 (1971).

[6]L. A. Firstein, J. M. Cherlow, and R. W. Hellwarth, Appl. Phys. Lett. 28, 25 (1976).

[7]K. B. Lyons and P. A. Fleury, to be published.

[8]N. F. Borrelli, Phys. Chem. Glasses 12, 93 (1971).

[9]P. A. Fleury and K. B. Lyons, in Proceedings of the Conference on Structure and Excitations of Amorphous Solids, Williamsburg, Virginia, 1976 (to be published).

[10]P. M. Selzer, D. L. Huber, D. S. Hamilton, W. M. Yen, and M. J. Weber, Phys. Rev. Lett. 36, 813 (1976).

[11]P. A. Fleury, Comments Solid State Phys. 4, 167 (1972).

[12]R. E. Strakna and H. T. Savage, J. Appl. Phys. 35, 1445 (1964).

[13]Similar observations have been noted regarding the absorption of far-ir radiation in glasses. See, for example, M. von Schickfus, S. Hunklinger, and L. Piche, Phys. Rev. Lett. 35, 876 (1975); and K. K. Mon, Y. J. Chabal, and A. J. Sievers, Phys. Rev. Lett. 35, 1352 (1975).

Evidence for Crossover Behavior near the Soft-Mode Transition in $SrTiO_3$ †

E. R. Domb, H. K. Schurmann, and T. Mihalisin
Department of Physics, Temple University, Philadelphia, Pennsylvania 19122
(Received 21 July 1975; revised manuscript received 6 October 1975)

A T_c-independent graphical analysis of the ultrasonic attenuation in $SrTiO_3$ shows evidence for a crossover behavior near the soft-mode transition. This crossover is believed to be from an essentially two-dimensional behavior far from T_c to a three-dimensional behavior very near T_c.

It is now well established[1] that systems undergoing a critical-point transition may be characterized as belonging to a particular "universality class." These classes are defined only by the system dimensionality and the symmetry of the order parameter. Phase transitions have identical critical exponents if they belong to the same universality class. Recently[2] it has been recognized that a substantial number of systems may in fact show critical behavior associated with two different universality classes as one approaches T_c. An example of this "crossover" behavior is in systems such as $KMnF_3$ and $SrTiO_3$ which undergo a soft-mode[3] structural transition. The order parameter in these systems is an angle of rotation of the F or O octahedra. Octahedra in the same plane are coupled much more strongly than octahedra in adjacent planes. As a result, the fluctuations are essentially two-dimensional until one gets very close to T_A.

Recently Schwabl[4] has developed a theory of ultrasonic attenuation for such systems which considers the interaction of the ultrasound not only with the soft phonon but also with the central peak observed[5] in neutron-scattering experiments. He predicts that the critical part of the attenuation α_c will go as $\alpha_c \sim \omega^2 \epsilon^{-\eta}$, where η is 1.25 near T_c and $\eta = 1.75$ far from T_c. Hence a log-log plot of α_c versus $\epsilon \equiv (T - T_A)/T_A$ is predicted to cross over from a strong form $\eta = 1.75$ far from T_A to a weaker divergence $\eta = 1.25$ near T_A. The form of the crossing over is not known.[4] Moreover, a crossing over from a strong divergence to a weaker one near T_A presents a difficult data-analysis task since this is in the same direction as rounding effects. Hence a search for crossover effects is complicated by two essential points: First, a fit by a known form over a wide range in ϵ is not possible; second, graphical techniques involving ϵ are risky since they are extremely sensitive to the choice for T_A.

Recently[6] we chose to look for evidence of crossover in $KMnF_3$ by using a null-hypothesis approach. Here data for several frequencies were successfully fitted by a single exponent for the range $0.001 < \epsilon < 0.1$; thus if crossover occurs, it must take place at $\epsilon < 0.001$ or $\epsilon > 0.1$. This approach for the longitudinal ultrasonic attenuation data on $SrTiO_3$ along (100) has failed. As a result, we sought a definitive positive test for crossover which would not be dependent on the choice of T_A.

A simple $\ln\alpha_c$-versus-$\ln\epsilon$ plot is potentially dangerous because of the sensitivity to T_A. Thus we have used a T_A-independent graphical method to search for crossover. The method is outlined below. One must assume that far from T_A the data are well represented by a single-exponent form $\alpha = A\epsilon^{-\eta} + B$. Here B is the background. Differentiating and taking logarithms one obtains

$$\ln\frac{d(1/\alpha_c)}{dT} = \text{const} + \frac{\eta - 1}{\eta}\ln\left(\frac{1}{\alpha_c}\right). \quad (1)$$

Thus a plot of $\ln[d(1/\alpha_c)/dT]$ versus $\ln(1/\alpha_c)$ should yield one straight line of slope $S = (\eta - 1)/\eta$ if no crossover occurs. However, if crossover is present one would expect a change in η and hence S. For example, taking Schwabl's prediction,[4] one would expect $S \sim 0.43$ far from T_A and $S \sim 0.2$ near T_A.

The pulse-echo technique was used to measure the attentuation to a precision of ± 0.02 dB for $\alpha < 2$ dB and to 2% for $\alpha > 2$ dB per echo. The technique was identical to that reported earlier[6] and allowed a temperature-measurement precision of ± 0.01 K. The sample was a "Gem" quality