Tunneling States and Resonant Light Interaction in an Oxide Glass

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A light scattering study has been performed on two efficient Raman scattering optical glasses from 0.15 to 3 THz at low temperatures. In the low-frequency range, we found an increase of the scattered intensity below 10 K. In contrast to previous investigations, mainly in vitreous silica, which have found an absence of light scattering by resonant interaction with two-level systems in glasses, our results are in good agreement with theoretical predictions which assume a coupling of light with tunneling states. [S0031-9007(96)00687-4]

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The low-temperature properties of glasses have been widely investigated in recent years. The behavior of amorphous solids at low temperatures differs completely from that of crystalline solids. At low temperature a number of anomalous effects have been observed and attributed to low energy excitations closely related to the amorphous state. Most of the differences observed between glass and crystal properties have been accounted for using a phenomenological description in terms of two-level systems (TLS) [1,2]. Despite the lack of a precise microscopic model for the origin of the TLS, it is possible to explain, assuming a tunneling of atoms or groups of atoms, the specific glass properties for temperatures lower than a few K. At higher temperatures the model has been extended towards soft configurations [3], or overdamped TLS [4]. Recently excited states of TLS have been proposed as an interpretation of infrared (IR) data [5].

The phenomenological tunneling model has been used successfully to describe a wide variety of thermal conductivity, specific heat, ultrasonic, and dielectric observations. The connection between these various physical properties has been extensively studied [6]. Theoretical relations have been also proposed to explain the connection between far infrared, ultrasonic absorption, and inelastic light scattering measurements [7]. Nevertheless, for these last properties the experimental verification is much less conclusive. In particular, the behavior of inelastic light scattering at low frequencies and low temperatures is not well understood. The early measurements of Winterling [8] have shown inelastic light scattering intensity in excess (ILSE) over the vibrational contributions (such as Debye density of states) in vitreous silica and various oxide glasses. This ILSE increases with temperature above the glass transition temperature T_g. The most relevant explanation for this feature ascribes it to relaxational processes due to quasiharmonic or anharmonic oscillators which are thermally activated at high temperatures. Attempts to observe the scattering from resonant interaction with TLS in silica fibers, which were chosen in order to enhance the weak scattered signal, were unsuccessful [9,10]. Thus the authors have concluded to the lack of direct scattering from TLS in vitreous silica. Very recently using low-frequency Raman investigation a glasslike behavior has been observed in fluorite mixed crystals [11].

In this Letter, we present the results of inelastic light scattering in two optical oxide glasses. In contrast to the preceding statement about SiO_2 we find, for the first time to our knowledge, an enhancement of the ILSE below 10 K, indicating a direct interaction of light with TLS. We analyze our results in the framework of the theoretical predictions of Theodorakopoulos and Jäckle (TJ) [12]. By comparing the LASF7 results with hypersonic attenuation in the same temperature range, we conclude the existence of two kinds of defects, differently coupled to the light scattering and to acoustic vibrations. Finally, we discuss a possible origin of the unsuccessful previous attempts.

We have studied two commercial optical glasses: a soda-lime-silica glass and a heavy metal oxide glass (labeled LASF7 from Schott company), which is known to be an efficient Raman scatter and was previously studied at lower frequencies and higher temperatures [13–16]. Stokes and anti-Stokes Raman spectra were measured in the right angle geometry with a conventional triple pass grating Coderg T800 spectrometer. The incident light was the 514.5 nm line of an argon-ion laser (Spectra Physics 2020) in multimode use. The resolution was about 1.5 cm^{-1}. The incident power on the sample was limited (200 mW) to avoid heating due to absorption related to the yellow color of the sample. The spectra were recorded in the $4-1500\ \mathrm{cm}^{-1}$ frequency range in vertical-horizontal (VH) polarization, at temperatures as low as 2 K and up to 300 K. In the cryostat used, the sample was cooled by circulation of ^{4}He gas. Below 4.2 K, the sample was immersed in a pumped liquid helium bath. The temperature of the gas was stabilized using a heater and a PID amplifier. The accuracy of temperature measurements was better than 1 K.

In Fig. 1, the frequency and temperature dependences of the Stokes side Raman spectra are plotted as $I_{RS}/\omega[n(\omega,T)+1] \equiv \chi(\omega,T)/\omega$, where $\chi(\omega,T)$ is the susceptibility and $n(\omega,T) = [\exp(\hbar\omega/kT) - 1]^{-1}$ is the Bose population factor. It should be noted that below 10 K the Bose factor in the Stokes spectrum is nearly equal to 1 in the low-frequency range investigated. Thus

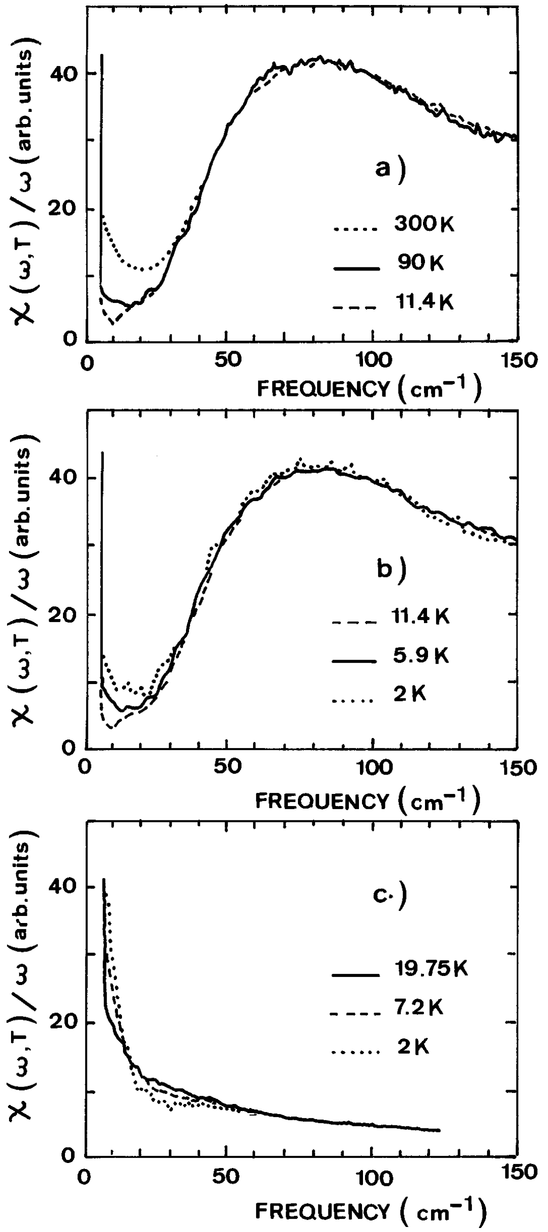

FIG. 1. (a) Reduced Raman intensity for LASF7 glass from 11.4 to 300 K, normalized to the high-frequency bands (the prefactors used are close to 1). (b) Reduced Raman intensity for LASF7 glass from 2 to 11.4 K. In the minimum, the intensity at 2 K is two times higher than at 11.4 K. (c) Reduced Raman intensity for soda-lime-silica glass from 2 to 19.7 K.

uncertainties of about 1 K in the temperature determination do not modify the reduced spectra as has also been checked explicitly. The spectra are normalized using the high-frequency part (from 100 to 1500 cm^{-1}), where spectral features coincide perfectly at any investigated temperature.

Figure 1(a) presents the normalized spectra for the high-temperature range (12–300 K) in LASF7 sample demonstrating that the intensity of the low-frequency part decreases with temperature more rapidly than predicted by the Bose population factor. This feature is in agreement with previous works in various glasses. In contrast, Fig. 1(b) shows that the normalized ILSE for the same sample is largest (for the 6–25 cm^{-1} range) at the lowest temperature. With increasing temperature, the magnitude of the quasielastic intensity decreases [Fig. 1(b)], reaching a minimum at about 12 K, and then increases again at higher temperatures [Fig. 1(a)]. The same data are plotted in Fig. 1(c) for a soda-lime-silica glass.

This result is, to our knowledge, the first observation in a glass of an increase of quasielastic intensity at low temperature. Such behavior has been predicted by TJ [12], assuming a coupling of light to the quantum-mechanical tunneling states of glasses. Arguing that the two configurations derive from states of different electric polarizability, TJ calculated the frequency and temperature dependence of the inelastic light scattering as a function of the density of the two-state defects $N(\omega)$. Two regimes should be considered. In the simplest case, where only one component of the polarizability tensor is nonzero, the resonant interaction for the depolarized Raman intensity is given by

$$\frac{I(\omega)}{\omega[n(\omega,T)+1]} \propto (\Delta\alpha)^2 \frac{1}{\omega} N(\omega) \tanh\left(\frac{1}{2}\hbar\omega/kT\right). \tag{1}$$

At higher temperature, relaxational processes across the barrier dominate:

$$\frac{I(\omega)}{\omega[n(\omega,T)+1]} \propto (\Delta\alpha)^2 \frac{1}{T} \int dV\, P(V) \frac{\tau(V)}{1+\omega^2\tau^2(V)}, \tag{2}$$

where $P(V)$ is the distribution of barrier height of the TLS, τ is the relaxation time, and $\Delta\alpha$ is the dielectric susceptibility variation.

To examine quantitatively the ILSE according to the TJ model, it is necessary to evaluate the contribution in the low-frequency range of scattering due to acoustic modes. This analysis concerns the LASF7 glass because its low-frequency anomalous behavior extends in a larger frequency range. In order to point out the anomalous thermal effect at low frequencies, Fig. 2 shows the behavior of $\chi(\omega)\omega$ in a semilogarithmic representation. As can be noted, for frequencies above 20–25 cm^{-1}, the relative change in the normalized intensity with temperature is quite small. By analogy with higher temperature analyzes, we have fitted the vibrational part which is dominant below 100 down to about 25 cm^{-1}, by a log-normal frequency dependence. The choice of this analytical form to describe the boson peak (observed near 80 cm^{-1} in this glass; see Fig. 1) has been largely discussed [17]. In fact, below the boson peak maximum, the shape of the fit is not very sensitive to the analytical form at low frequencies. Moreover, we also found that the fit does not depend crucially on the precise choice of the upper cutoff frequency. Figure 2(b) gives an example of such a fit. A similar shape is observed with the IR absorption [18].

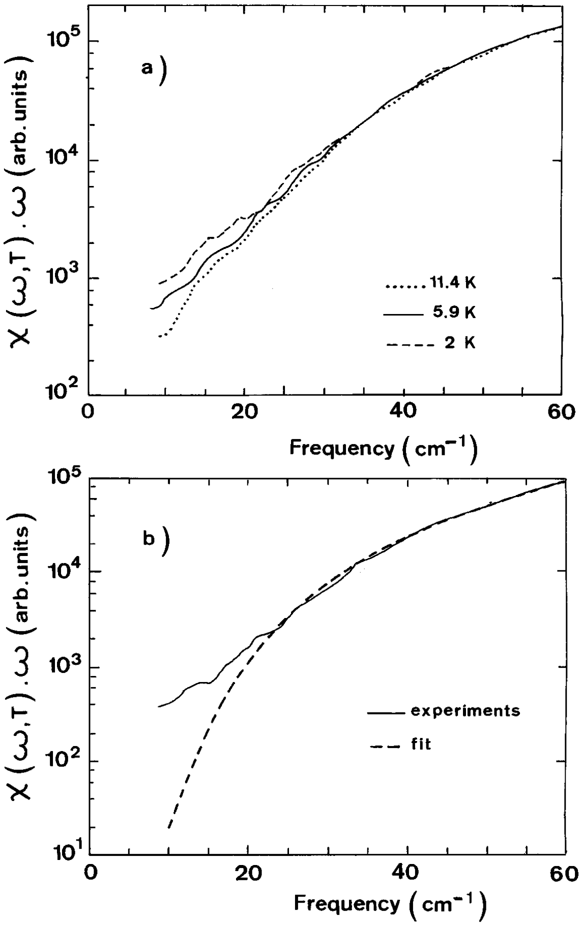

FIG. 2. (a) Semilogarithmic representation of the susceptibility multiplied by the frequency $\chi(\omega,T)\omega$ versus frequency for the low temperatures. (b) Example of the curve fitted to the $\chi(\omega,T)\omega$ spectrum (14.5 K), using a log-normal formula for describing the vibrational contribution (dashed line). The solid line represents the experimental data. The relaxational contributions are dominant in the frequency range below 20 cm^{-1}.

A departure of the experimental data from the fit curve is evident at low frequencies. The quasielastic contributions are the most important at these frequencies, while the vibrational contributions appear negligible below 12–13 cm^{-1}. The variation with temperature can be now quantitatively compared to TJ predictions. To be sure that the contributions from the elastic component are completely removed, we have considered only data above 6 cm^{-1}. Note that the full width of the apparatus function of the spectrometer is 1.5 cm^{-1}, and that the elastic intensity is independent of the temperature.

Figure 3 shows the temperature dependence of the scattered intensity at two frequency shifts. The solid lines result from applying Eq. (1) for the normalized Raman scattering intensity at two frequencies 6 and 13 cm^{-1}, respectively. The fit to the experimental data is in reasonable agreement below 10 K, including the plateau at very low temperatures. More remarkable, the single adjustable fit parameter for the amplitude is the same at both frequencies. So, the frequency and temperature dependencies of the Raman spectra for temperature lower than 10 K are well accounted for by the TJ model.

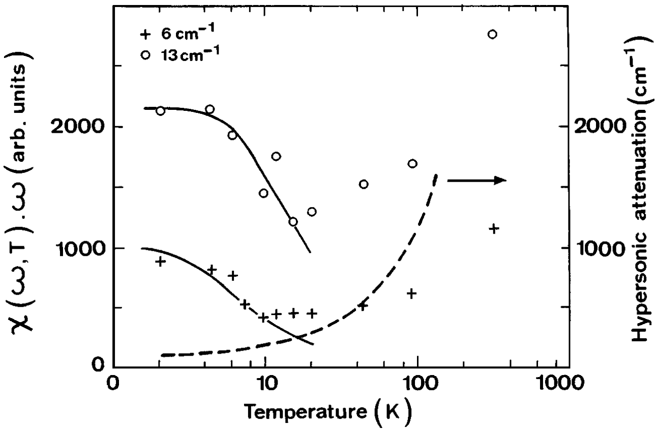

FIG. 3. Evolution of experimental TLS and relaxational contribution to the $\chi(\omega,T)\omega$ spectra. They are presented as a function of temperature at two frequencies shift. The solid line results from fitting procedure using the TJ model Eq. (1) for very-low-temperature range (full lines). The hypersonic attenuation is extracted from Ref. [14] (dashed line).

The low-temperature features of light scattering can thus be well represented by quantum-mechanical tunneling states. However a clear discrepancy develops above 10–20 K, cf. Fig. 3. Indeed the crossover from the resonant interaction regime to the thermal relaxation process has given rise to the introduction of conflicting models [19]: soft potential model [20], influence of higher excited levels of TLS [5], overdamping of TLS [4] have been considered. Hitherto only poor agreement has been found between theoretical predictions and experimental results at temperatures above a few kelvin.

Therefore, we consider now the high-temperature regime which can be interpreted in terms of incoherent scattering of light by defects which relax via classical thermal activation. These are the same defects which cause the high-temperature peak ($T = 50{-}100$ K) in the ultrasonic attenuation. TJ have proposed such a calculation, Eq. (2), using a barrier distribution $P(V)$ for which all parameters needed can be derived from ultrasonic data (typically 100 MHz). To describe the Raman quasielastic intensity, Eq. (2) is then extrapolated to higher frequencies (0.1–0.3 THz). The calculated temperature dependence agrees reasonably well with the experimental results for vitreous silica at temperatures not higher than room temperature, but fails in other glasses [21]. This procedure has also been tested in LASF7 glass but only at room temperature [16] and has failed once again.

In order to evaluate the Raman scattering intensity I_R various analytical forms have been proposed for the potential barrier distribution $P(V)$ to be deduced from ultrasonic measurements. In particular, TJ have chosen a Gaussian distribution, while Buchenau *et al.* [22] and

Gilroy and Phillips [23] have used other forms and have found better agreement in the silica case.

This procedure supposes that the same defects are responsible for acoustic attenuation and Raman scattering intensity. If this assumption is valid, the connection will be obviously better if one considers directly the hypersonic attenuation measured at a frequency which is close to the Raman frequencies. The latter comparison has already shown to work for silica and B_2O_3 [7,24], and in an optical glass at high temperatures [25].

Instead of comparing the ultrasonic attenuation ℓ^{-1} at 100 MHz with the Raman intensity, it would be better to check the relationship $I_R \propto \ell^{-1}$ [7] using hypersonic attenuation at 30 GHz. Indeed, this procedure avoids the extrapolation of Eq. (2) to frequencies which are 3 orders of magnitude higher. In Fig. 3, we have included the hypersonic attenuation of LASF7 glass $\ell^{-1}(T)$ at 1 cm^{-1} from previous work [16]. Considering the full temperature range, a striking disagreement is observed. This experimental result seems to reveal that the nature of the defects responsible for the hypersonic, and for the Raman scattering properties, differs in LASF7 glass. This is at variance with the findings in vitreous silica. It has already been noted that different kinds of defects are active depending on whether one considers dielectric or acoustic properties [26]. In particular, the influence of OH content in silica glasses has been extensively studied. On the other hand, a considerable dependence of the polarizability, responsible for the Raman intensity, on the composition of the glasses has been found, whereas the hypersonic attenuation depends only slightly on the chemical nature of the sample: ℓ^{-1} is approximately 100 cm^{-1} at 2 K for both LASF7 and silica. Furthermore, the distribution of energy $N(\omega)$ deduced from velocity variation with temperature differs only by a factor of 2 in LASF7 compared to vitreous silica [16]. All these data suggest that two kinds of defects coexist or/and are coupled differently to the acoustical phonons and light scattering, especially in LASF7 glass. Moreover, results in progress performed on soda-lime-silica glass exhibit the same anomalous Raman intensity increase at very low temperatures, underlying that this effect is not specific to LASF7 glass. The intensity variations of the soda-lime-silica present some similarities and some differences with these observed in LASF7. Firstly, although the relaxational/vibrational intensity ratios of the two glasses are different, the resonant interaction at low frequencies is once again observed suggesting a universal behavior. Secondly, at about 15 cm^{-1} a crossover is observed, as in IR measurements reported recently in the same kind of glass [5]. Excited state transitions of the TLS have been postulated to explain this behavior. Finally, as the hypersonic attenuation is not available up to now in this glass, comparison cannot be made to conclude about the nature of the defects. These results will be presented in a forthcoming publication [27].

The distinction between the two kinds of defects induces probably some consequences which have not been taken into account so far in the comparison between Raman scattering measurements and other relevant experimental results such as neutron scattering [28].

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