## Low-Energy Modes in Phosphate Glasses: A Comparison with the Soft Potential Model

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Low-frequency Raman spectra of samarium phosphate glasses  $(Sm_2O_3)_x(P_2O_5)_{1-x}$  obtained over a wide temperature range 11–973 K, were compared with those of low-temperature specific heat. The temperature and frequency dependencies of the quasielastic scattering and boson peak, as well as the anomalous specific heat, agree qualitatively with predictions of the soft potential (SP) model. The "excess" spectral density may also be consistent with SP predictions, assuming (1) comparatively high phonon spectral density, and (2) approximately linear in frequency light-soft mode coupling. However, these assumptions are in conflict with recent formulations of the theory.

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There are striking characteristics in the low-frequency vibrational states of glasses that are absent in the corresponding crystalline solid [1,2]. At temperatures below ~1 K, localized low-frequency vibrations, successfully described in terms of two level systems [3], cause an excess in the specific heat, scatter phonons, and lower markedly the thermal conductivity. This results in linear specific heat and quadratic thermal conductivity temperature dependencies. Above 1 K a further excess of the specific heat over that predicted by the Debye theory is demonstrated in a bump in the  $C_p/T^3$  plot, and it is believed to arise from additional localized soft harmonic modes [2]. The latter introduce a contribution to the phonon density of states and have been revealed by inelastic neutron scattering measurements [2]. They interact strongly with acoustical phonons [4-6] and are thought to cause the observed plateau in the thermal conductivity temperature dependence. It is likely that these soft modes also are related to effects observed in low frequency infrared absorption [7] and Raman scattering [2,8]. In particular, Raman spectra of glasses show in the low-frequency region (below 100 cm<sup>-1</sup>) two features not present in crystalline systems: quasielastic scattering (QS) in the region below 15  $cm^{-1}$ and a broad band observed in the range  $20-100 \text{ cm}^{-1}$  the boson peak (BP) [9,10]. The former increases in intensity with temperature at a higher rate than the Bose population factor, while the latter contribution usually follows the Bose temperature behavior. Consequently, it is possible to evaluate the contribution from each of the two spectral features by taking their different temperature behaviors into account. At sufficiently low temperatures (<20-50 K) the QS is weak enough to be neglected, and we can focus the attention on the BP. In general, first-order Raman scattering in a disordered system reflects, in the harmonic approximation, the vibrational density of states  $g(\omega)$  modulated by the coupling function  $C(\omega)$  [11]:

$$I^{\exp}\omega/[n(\omega,T)+1] = C(\omega)g(\omega).$$
(1)

It is known that the complexity of the vibrational characteristics of a disordered system can affect both the functions  $g(\omega)$  and  $C(\omega)$  [12]. Martin and Brenig [13] have suggested that the lack of periodicity in amorphous structure induces electrical and mechanical disorder, which gives rise to spatial fluctuations in the photoelastic and elastic constants such that the BP can be attributed to a peak in the coupling function  $C(\omega)$ , taking the density of states  $g(\omega)$  proportional to  $\omega^2$ . Neutron scattering measurements reveal, however, that the BP is caused by a peak in  $g(\omega)$  rather than in  $C(\omega)$  [14–16].

In the later models it is suggested that the BP occurs due to crossovers in the vibrational density of states from propagating phonons at low frequencies either to a phonon localized regime due to strong scattering of phonons with wavelengths comparable to the length scale of static density fluctuations in the intermediate range (5– 50 Å) [17] or to a regime of fractal dynamics (fractons) at higher frequencies [18–20].

The models discussed above give, however, only qualitative phenomenological descriptions of the BP and, furthermore, do not consider the existence of QS. A model which addresses the QS has been proposed by Jäckle [8] and attributes it to structural relaxation of double well potential defects with different polarizabilities. The microscopic origin of QS should then be the same as that which causes the acoustic attenuation peaks revealed above 20 K in glasses [21–23]. This model provided a successful interpretation of Raman scattering data in vitreous silica [8], but was unable to describe quantitatively experimental results for other glasses [24].

It is likely that the various anomalous vibrational states of glasses, including the tunneling states, have a common microscopic origin and cause both the QS and the BP. An attractive model has been proposed to account for the excess density of states in terms of localized vibrations which arise from soft anharmonic potentials (SP) with a random distribution of characteristic parameters [25,26].

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The SP model provides a unitary explanation for *both* the tunneling and low-frequency vibrational states and, in particular, it attributes the QS and the BP to the modulation of the local dielectric susceptibility due to localized soft vibrational modes [27]. The SP approach postulates that anharmonic soft double- and single-well potentials characterize a glassy network. Corresponding excitations are coupled to acoustical phonons, the interaction being either resonant or nonresonant ("relaxation").

In this model, the experimental intensity of the Raman scattering from the soft modes can be written as:

$$I_{\exp}(\omega,T) \propto ([n(\omega,T)+1]/\omega)l^{-1}(\omega,T).$$
 (2)

Here  $l^{-1}$  is the inverse mean free path of acoustical phonons and reflects the interaction between the phonons and the soft modes. Taking into account different mechanisms involved, in the range of frequency probed by Raman scattering it splits into:  $l^{-1} =$  $(l^{-1})_{\text{rel},DW} + (l^{-1})_{\text{rel},SW} + (l^{-1})_{\text{res},SW}$  within the limit  $\hbar\omega, kT \gg W$  (W represents, in the SP model, a characteristic energy of the order of  $2-5 \text{ cm}^{-1}$ ). Here  $(l^{-1})_{res,SW}$  represents the temperature independent resonant processes in a single well, whereas  $(l^{-1})_{rel,DW}$ and  $(l^{-1})_{rel,SW}$  represent the temperature dependent relaxation processes of a double and single well, respectively. The latter can be expressed as  $(l^{-1})_{\text{rel},DW} = (\pi \omega C/\nu)(kT/W)^{3/4}ln^{-1/4}(1/\omega\tau_0)$  with  $C = P_0 \underline{H^2 W/V}$  $\rho v^2 \sqrt{\eta_L}$  and  $(l^{-1})_{\text{rel},SW} = (16/9)(C\omega kT/vE_c)\sqrt{W/\hbar\omega}$ with  $E_c = \sqrt{2\pi\rho\hbar^3 v^5}/(HW/\eta_L^{3/2})$ . Here  $H(\sim 1)$  and  $\eta_L(\sim 10^{-2})$  are dimensionless coefficients, v is the sound velocity, and  $\rho$  is the density. These relations are valid up to a certain energy, determined by  $\hbar \omega_d = (0.6 - 0.8) W C^{-1/3}$ , above which sound waves mix strongly with the soft modes. For  $\omega > \omega_d$  the local quasiharmonic excitations cannot be regarded as independent, and as a result the Raman intensity decreases with frequency,  $I(\omega, T) \propto n(\omega, T) + 1$ , which then defines the high-frequency part of the BP. However, in the low-frequency range  $\omega < \omega_d$  the SP model gives specific predictions. According to Eq. (2), the Raman scattering intensity from the soft modes should follow a  $T^{0.75} - T^{1.0}$ behavior (excluding the trivial population factor which is  $\propto T$ ).

It is the aim of this Letter to determine the frequency dependence and the temperature evolution of the lowenergy modes in the glassy state by using a combination of low-frequency Raman scattering performed over a wide temperature range and low temperature specific heat measurements.

We chose to investigate samples of the samarium phosphate  $(Sm_2O_3)_x(P_2O_5)_{1-x}$  glass system, since the glass transition temperature  $(T_g \approx 910 \text{ K})$  is high and thus allows a large temperature range to be investigated. The Raman experiments were performed in the range 11–1100 K. For the same set of glasses specific heat [28] and

ultrasonic measurements [29] have been performed, so the complete set of parameters used in SP is available.

We present in Fig. 1 depolarized (HV) Raman spectra, reduced for the Bose-Einstein population factor  $n(\omega, T)$  + 1, at selected temperatures for a  $(Sm_2O_3)_{0.25}(P_2O_5)_{0.75}$ glass in a log-log representation (similar behavior was found in a glass of different molar fraction x of samarium oxide x = 19%). For the two highest temperatures a constant background caused by higher order scattering processes has been subtracted. Details will be described elsewhere [30]. As seen in Fig. 1, the intensity in the lowfrequency ( $< 25 \text{ cm}^{-1}$ ) range increases much faster with increasing temperature than the Bose population factor. The intensity increase is largest for the lowest frequency investigated, indicating that this contribution is quasielastic in nature (i.e., centered around zero frequency). In the inset of Fig. 1 we show the temperature dependence of the intensity at one of the lowest frequencies probed  $(8 \text{ cm}^{-1}, \text{ being well below the BP frequency})$  in a log-log plot. The intensity is well fitted by a power law,  $I \propto T^{\alpha}$ , with exponent  $\alpha \approx 0.5$  over the whole temperature range 11-973 K. In the figure we also depict results obtained in our laboratory for other phosphate glasses, as well as for GeO<sub>2</sub> and SiO<sub>2</sub> [31]. The exponent  $\alpha$  appears to be material dependent and varies in the range 0.5-1.3 for these glasses. The exponents, although material dependent, are close to the SP prediction of  $\alpha = 0.75 - 1$  [see Eq. (2)].

Having established that the temperature dependence of the QS roughly follows the SP predictions, we now turn to the vibrational modes, as manifested in the BP. In the SP these are described by the resonant form  $(l^{-1})_{\text{res},SW}$ .



FIG. 1. Log-log plot of low-frequency Raman spectra  $I(\omega)/[n(\omega,T) + 1]$  of samarium phosphate glass  $(Sm_2O_3)_{0.25}(P_2O_5)_{0.75}$  at temperatures indicated by the legends. Full line indicates a power-law behavior of the lowest temperature spectrum with exponent 2.8. Inset: log-log plot of Raman scattering intensity at 8 cm<sup>-1</sup> vs temperature (circles, full line). Dashed lines indicate corresponding behavior of some other glasses: Eu<sub>2</sub>O<sub>3</sub>:P<sub>2</sub>O<sub>5</sub> (1), GeO<sub>2</sub> (2), Gd<sub>2</sub>O<sub>3</sub>:P<sub>2</sub>O<sub>5</sub> (3), AgI:AgPO<sub>3</sub> (4), and SiO<sub>2</sub> (5).

This excess density of states above the Debye contribution should then also be manifested in the low temperature specific heat as a peak in a  $C_p/T^3$  vs T plot at low temperatures ( $\sim 10$  K). The density of quasiharmonic soft modes in the SP model [27] is predicted to obey an  $\omega^4$ frequency dependence below the Bose peak maximum. This behavior has its counterpart in the specific heat as a  $T^5$  dependence below the peak in  $C_p/T^3$  vs T. From Fig. 1 it can be seen that in the low-frequency range  $(8-30 \text{ cm}^{-1})$  the lowest temperature spectrum, for which the QS is suppressed, follows a power law behavior  $\propto \omega^{2.8}$ , i.e.,  $C(\omega)g(\omega) \propto \omega^{3.8}$ . However, it is not possible to directly determine  $g(\omega)$  from the lowfrequency Raman scattering due to the modulation by the coupling function  $C(\omega)$  [see Eq. (1)]. A reasonable estimate of  $C(\omega)$ , and hence also of  $g(\omega)$ , can be made using low temperature specific heat data. Assuming a specific frequency dependence  $C(\omega) \propto \omega^a$ ,  $C_p$  can be calculated from  $I(\omega)$  using the relation

$$C_p \approx C_v = 3N \int_0^{\omega_0} g(\omega) \hbar \omega \frac{\partial n(\omega, T)}{\partial T} d\omega$$
, (3)

where N is the number density,  $\omega_0$  is the highest vibrational frequency, and  $n(\omega, T)$  is the occupation number. By comparing the results calculated from the Raman spectrum using different exponents a with the experimentally determined temperature dependence of  $C_p$ , an estimate of  $C(\omega)$  [and then  $g(\omega)$ ] is obtained. In Fig. 2 we present low-temperature  $C_p$  data for the present glass in a  $C_p/T^3$  vs T plot to facilitate a comparison with Debye behavior (dashed horizontal line). As is common for glasses, a peak is readily observed at about 10 K, indicating excess modes as compared to Debye behavior. The peak value is more than 2 times larger than the Debye contribution calculated from the sound velocities. In the



FIG. 2. Specific heat data for  $(Sm_2O_3)_{0.25}(P_2O_5)_{0.75}$  glass. Horizontal line indicates the Debye value calculated from the sound velocity data [29]. Other curves represent fit results of Eq. (3) to the data using density of states from the lowest temperature Raman spectrum and different assumptions of  $C(\omega)$ , as indicated by the legends.

figure we include results for  $C_p$  calculated from the low-frequency Raman data, as indicated above, for various assumptions of a (a = 0.0, 0.6, 0.8, 1.0).

From the figure it can be seen that  $C(\omega) \propto \omega^{0.8}$ results in a reasonable description of the  $C_p(T)$  data. The resulting frequency dependence of  $C(\omega)$  is in sharp contrast with the general assumption of SP that the soft mode configuration does not depend on its eigenfrequency [25], which leads to a frequency independent  $C(\omega)$ . It is clear from Fig. 2 that  $C(\omega) = \text{const}$  cannot describe the data. Similar findings for  $C(\omega)$  were recently reported for other glasses [32].

The obtained  $C(\omega) \propto \omega$  then implies that  $g(\omega) \propto \omega^{2.8}$ , i.e., a frequency dependence that is larger than Debye behavior  $\omega^2$ , but less than the  $\omega^4$  dependence predicted by SP for the quasiharmonic modes. Thus SP seems to overestimate the excess density of states. A similar conclusion can be made from the  $C_p$  data (see Fig. 2). The low-temperature data, below the peak in  $C_p/T^3$ , follows approximately a  $C_p \propto T^{3.6}$  dependence while the soft quasiharmonic modes of SP are predicted to give a  $T^{\frac{1}{5}}$  contribution. It should be noted that the peak in  $C_p/T^3$  vs T resides on a background level (Fig. 2), which can almost be identified with the Debye contribution calculated from the sound velocity data. The minimum in  $C_p/T^3$  around 2 K, which separates the contributions of the excess vibrational modes from those of the well-known two-level systems, is just barely above the Debye level. Assuming that the excess modes are distinctly different from Debye modes, this suggests that the modes coexist with ordinary sound waves. As the Debye contribution dominates  $C_p$  around 2 K, then the sound waves may dominate  $g(\omega)$  about a few cm<sup>-1</sup>.

Assuming that the excess modes are distinctly different from phonons and that they coexist with sound waves, we may subtract the Debye density of states (calculated from sound velocities) from the density of states deduced from the comparison of Raman scattering and  $C_p$  data. In Fig. 3 we show the resulting density of states of the excess modes. The data in the low-frequency range < 25 cm<sup>-1</sup> are indeed in accordance with a  $(\omega - W)^4$  dependence, as predicted by SP for the soft quasiharmonic modes. Following a similar procedure for  $C_p$ , i.e., subtracting the Debye contribution, leads to a temperature dependence which is consistent with the  $T^5$  dependence predicted by the SP.

In conclusion, we have shown that low-frequency Raman scattering data over a broad temperature range and low-temperature specific heat data of a samarium phosphate glass in some aspects are in qualitative agreement with the soft potential model. Quantitative agreement is found for the temperature dependence of the low-frequency Raman data. By assuming that soft modes coexist with sound waves of comparable density, as is suggested by the data, even quantitative agreement is found for the frequency dependence of the



FIG. 3. Density of excess modes vs frequency as determined from the Raman spectrum, assuming  $C(\omega) \propto \omega^{0.8}$  and subtracting a Debye contribution calculated from the sound velocities [29]. Solid line represents the SP prediction  $\propto \omega^4$ , and dashed line represents Debye density of states.

Raman intensity and the temperature dependence of the specific heat data. However, the analysis clearly reveals that the light-vibration coupling constant is frequency dependent (approximately, linear). This contradicts the general SP assumption that the soft mode configuration does not depend on its eigenfrequency [25], which leads to the conclusion that both the phonon-soft mode coupling and the light-soft mode coupling are frequency independent. Also, an existence of relatively high phonon spectral density is not compatible with recent formulations of the phonon-soft mode interaction problem [25].

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