

# Fast relaxation, boson peak, and anharmonicity in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses

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Glasses with a composition  $x\text{Li}_2\text{O}\cdot(1-x)\text{B}_2\text{O}_3$  were investigated by low-frequency Raman scattering in the composition range  $x=0-0.28$ . The evolution of the quasielastic line, the boson peak, the Debye frequency, and some other glass parameters with the composition was analyzed. The frequency of the boson peak  $\omega_b$  shifts with changing  $x$  by a factor of 3 and the width of the quasielastic spectrum at room temperature is always equal to  $\sim 0.24\omega_b$ . The Grüneisen parameter of the glasses is estimated on the basis of the light scattering data for the boson peak frequency within the frames of the anharmonic model of the fast relaxation and using the sound velocity data—for the Debye frequency. The anharmonic properties are compared with the fragility of these glassformers; it is shown that the fragility increases with anharmonicity. It is shown also that the width of the glass transition region correlates with the anharmonic properties. © 2000 American Institute of Physics. [S0021-9606(00)70939-1]

## I. INTRODUCTION

Low-frequency Raman scattering spectra in glasses exhibit two characteristic features: the boson peak in the THz region and the quasielastic line with a characteristic width on the order of a few hundreds GHz.<sup>1</sup> The former arises due to excess vibrations with a characteristic length on the intermediate range scale and the latter, due to fast relaxation processes. There is still no commonly accepted theory of these glass features. For the boson peak there are some phenomenological models<sup>2-9</sup> and computer simulation results.<sup>10,11</sup> Recently, a theory which predicts the boson peak was proposed.<sup>12</sup> Fast relaxation was attributed to the thermally excited transitions in the double well potentials,<sup>13,14</sup> to the anharmonicity of vibrations<sup>15</sup> or to fluctuations of the dynamical free volume holes.<sup>16</sup> Recently, a significant progress was achieved in understanding the fast relaxation in glasses after applying tandem Fabry-Perot technique for measuring the broadband (1–600 GHz) relaxation spectra.<sup>17-21</sup> In particular, it was shown that in glassy silica the fast relaxation process is caused by thermally activated jumps in the double well potentials at least up to the room temperature,<sup>21</sup> while in boron oxide glass the anharmonicity of the vibrations may be the dominant contribution.<sup>20</sup> In the latter case the quasielastic light scattering (QELS) apparently has a vibrational nature, i.e., it is a relaxational part of the vibrational response function. It means that the QELS spectrum should have some connection with the most prominent part of the acoustical spectrum—the boson peak. However, no systematic study of such connection is known.

Lithium borate glasses provide very good opportunity to check the correlation of some glass properties with the boson

peak and QELS and between both of them because the frequency of the boson peak changes very strongly with  $\text{Li}_2\text{O}$  fraction; the shift of the boson peak by a factor of 3 was reported<sup>22</sup> for lithium borate glasses. Fragility of these glassformers also demonstrates a strong dependence on the lithium fraction.<sup>23</sup> It was shown that there is a correlation between the QELS, boson peak, and fragility in various glassformers<sup>24</sup> which is still unexplained. The purpose of this paper is to analyze the behavior of the boson peak and QELS in a series of the lithium borate glasses of different composition and to check the possible correlations between them and other properties of the glasses.

## II. EXPERIMENT

### A. Samples

A series of lithium borate glasses of the composition  $x\text{Li}_2\text{O}\cdot(1-x)\text{B}_2\text{O}_3$  was prepared at regular intervals of 0.02 mole fraction through the composition range  $0 \leq x \leq 0.28$ . An

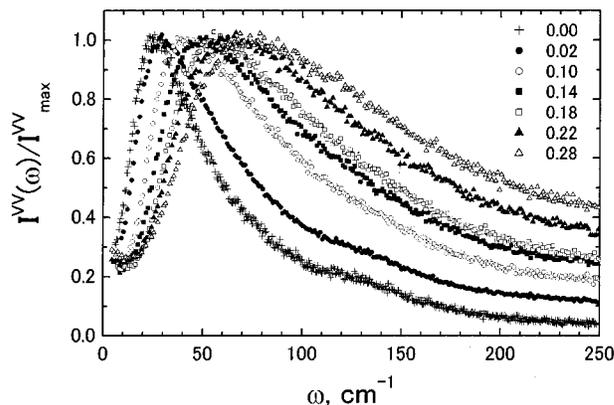


FIG. 1. The boson peak in lithium borate glasses of various composition  $x$ .

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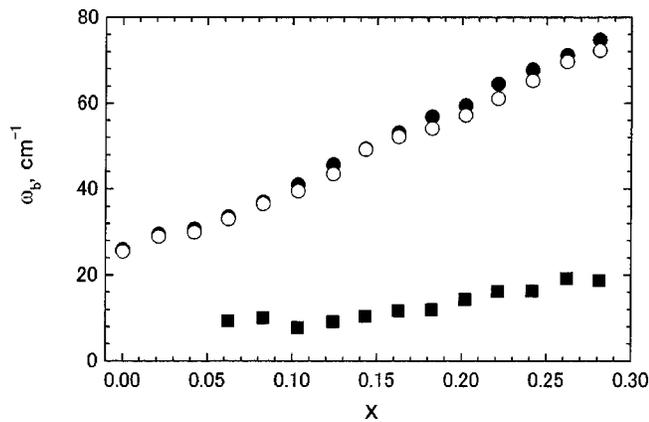


FIG. 2. Boson peak frequency in VV (solid circles) and VH (open circles) scattering. Solid squares, the width of the QELS  $\tau^{-1}$ .

attempt was made to prepare bulk glasses with higher  $x$ , up to  $x=0.36$ , but all of their respective melts crystallized quickly after casting. Analytical reagent grade  $\text{LiOH}\cdot\text{H}_2\text{O}$  (of purity greater than 99.0%, the main residue is lithium carbonate) and  $\text{H}_3\text{BO}_3$  (of purity greater than 99.7%) were used as the starting materials. The details of the sample preparation are described elsewhere.<sup>25</sup>

### B. Measurements

The room temperature Raman scattering was measured using an Ar ion laser with the power 50 mW, an additive triple-grating spectrometer Joben Yvon, and a photon counting system. The samples were immersed in silicone oil with a quartz optical cell of 15 mm  $\times$  15 mm  $\times$  20 mm to prevent them from absorbing moisture from the air. Both polarized (VV) and depolarized spectra (VH) are measured in a back-scattering geometry in the frequency range 5–300  $\text{cm}^{-1}$ .

## III. RESULTS AND DISCUSSION

### A. Boson peak

In Fig. 1 the polarized (VV) spectra of the boson peak are shown for a series of composition  $x$ . The amplitude is normalized to unity at the maximum of the boson peak. For  $x$  from 0 to 0.28 the frequency of the maximum of the boson peak,  $\omega_b$ , increases by a factor  $\sim 3$ , from 25 to 79  $\text{cm}^{-1}$  (Fig. 2). However, the spectral shape of the boson peak remains the same at all  $x$ ; in Fig. 3 the combined plot obtained by scaling the frequency on the frequency of the maximum  $\omega_b$  for each composition is shown. All curves coincide well except a small shoulder near  $\omega/\omega_b \sim 3.7$  which gradually decreases with increasing  $x$ .

It is known that increase of the mole fraction of  $\text{Li}_2\text{O}$  in lithium borate glasses leads to a significant increase of sound velocities and density.<sup>25</sup> Since the boson peak is in acoustical region of the vibrational spectrum, one can suspect that its shift with the change of the composition is a trivial one and arises merely due to the change of the average elastic constants and density. In this case it should shift just like, e.g., the Debye frequency  $\omega_D$ . We compared the dependence of  $\omega_b$  and  $\omega_D$  on  $x$ . The Debye frequency

$$\omega_D = v_D (6\pi n)^{1/3} \quad (1)$$

[where  $v_D = (2/v_t^3 + 1/v_l^3)^{-1/3}$  is the Debye velocity] we estimated using the data on the transversal ( $v_t$ ) and longitudinal ( $v_l$ ) sound velocities and particle density  $n$  from Ref. 25. For the reader's convenience we plot these data in Fig. 4. In Fig. 5 the dependence of  $\omega_b$  and  $\omega_D$  on  $x$  is shown. To make the comparison clearer we normalized the frequencies by their values at  $x=0$ . Figure 5 shows that the relative shift of the boson peak is faster than that of the Debye frequency (except a small interval  $x < 0.05$ ): both depend on  $x$  linearly but the slope is equal to 6.9 for  $\omega_b(x)/\omega_b(0)$  and 4.3 for  $\omega_D(x)/\omega_D(0)$ . In particular, at  $x=0.28$  the shift of the nor-

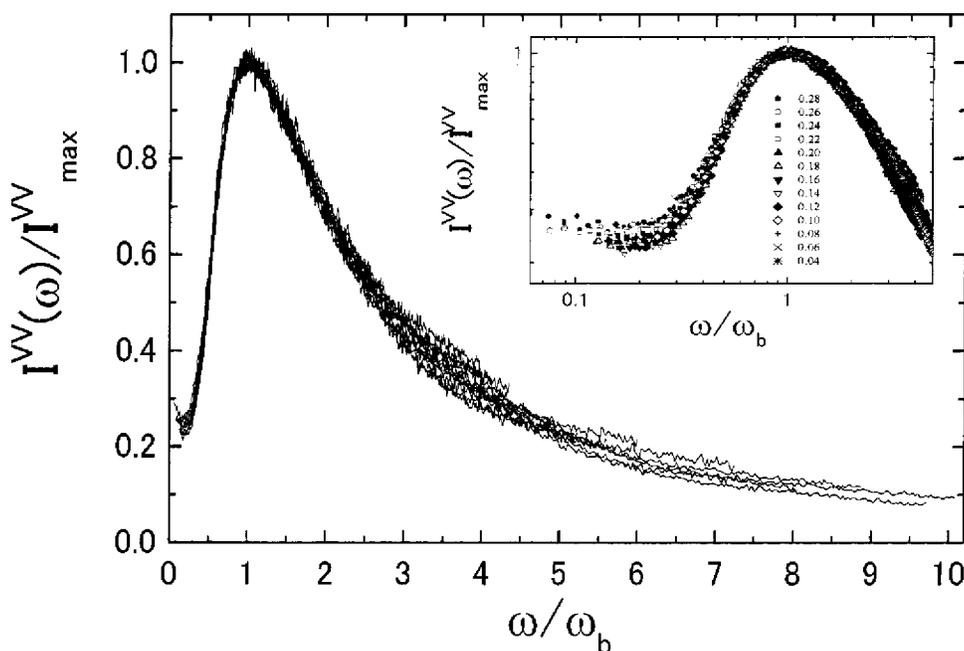


FIG. 3. The scaled boson peak spectra for all compositions  $x$ . Inset: log  $\omega$  plot of a part of the boson peak.

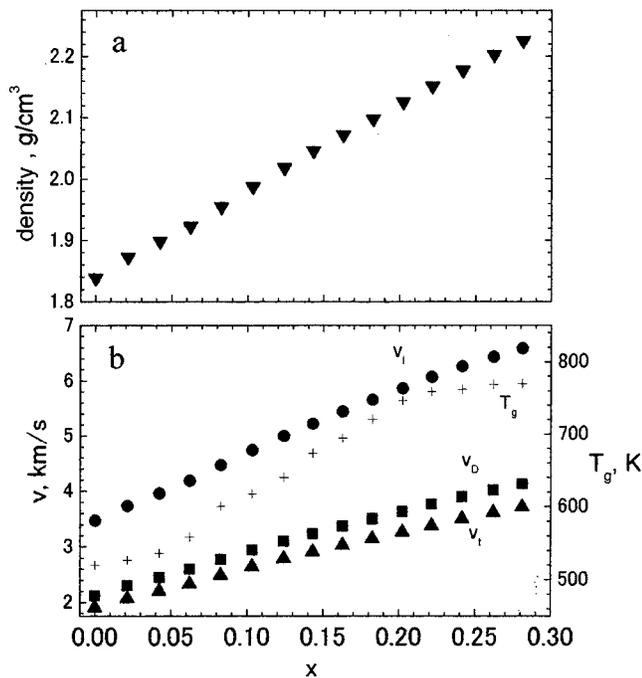


FIG. 4. Some parameters of the lithium borate glasses used in the paper: (a) density; (b) longitudinal (solid circles), transversal (solid triangle) sound velocities and glass transition temperature (cross). The data are from Ref. 25. Solid squares, Debye velocity.

normalized Debye frequency is by 30% lower than that of the boson peak. This means that the evolution of the boson peak is different from one determined by scaling of the elastic constants and density; the shape of the full acoustical spectrum changes and mirrors more rapid evolution of the boson peak in comparison with the higher frequency acoustical vibrations. We note that at  $x < 0.05$  some other properties of the lithium borate glasses behave differently from those at  $x > 0.05$  (see, e.g., Figs. 6, 9, and 11).

Sound velocity and frequency define a characteristic length,  $L \sim v/\omega$ . For the Debye frequency this length is of the order of the minimum possible acoustic wavelength determined by the interatomic distance. For the boson peak this length, which is a few times longer, should correspond to some structure features which are responsible for the appear-

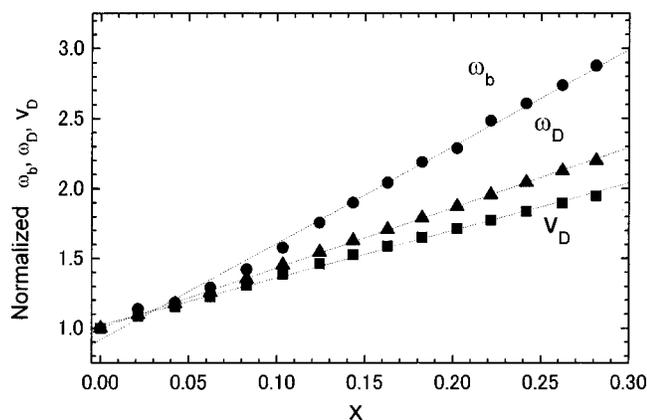


FIG. 5. Boson peak frequency (solid circles), Debye frequency (solid triangles), and Debye velocity (solid squares) normalized to 1 at  $x=0$ .

ance of these excess acoustical vibrations. This may be the size of the typical structure nanoheterogeneities,<sup>2-4</sup> or correlation length of the structure,<sup>5-7</sup> or a size of the soft-potential atomic configurations.<sup>8</sup> In silica glass the boson peak vibrations were identified with a specific motion of the a few connected  $\text{SiO}_4$  tetrahedra.<sup>9-11</sup> In any case, for the boson peak  $L$  corresponds to a medium-range scale important for characterization of structure correlations in glasses. In Fig. 6 a characteristic length defined as

$$L_b = v_D / \omega_b \quad (2)$$

is shown as a function of composition for the lithium borate glasses. The length  $L_b$  decreases from 2.7 to 1.9 nm, i.e., by the factor 1.42, in the interval  $x=0-0.28$ . However, the decrease of  $L_b$  itself does not necessary means the decrease of the extent of the medium-range correlations in the glass, because the density of the samples increases with  $x$ . To characterize the behavior of the structure correlations one needs to compare the decrease of  $L_b$  with the behavior of a length which characterizes the average interparticle distance. The latter can be defined as  $a(x) = (\rho(x)/M(x))^{-1/3}$ , where  $M(x) = xM_{\text{Li}_2\text{O}} + (1-x)M_{\text{B}_2\text{O}_3}$ ,  $M_{\text{Li}_2\text{O}} = 29.8M_{\text{au}}$ , and  $M_{\text{B}_2\text{O}_3} = 69.62M_{\text{au}}$  are the respective molar masses,  $M_{\text{au}}$  is the atomic mass unit. The dependence of  $a$  on  $x$  is shown in Fig. 6 (inset b); it is a perfect linearly decreasing function. On the inset a in this figure the ratio  $L_b/a$  is shown. This ratio decreases more or less monotonically from 6.8 at  $x=0$  to 5.2 at  $x=0.28$ . Thus,  $L_b$  decreases not only in absolute value (by 42%), but also in units of interatomic distance (by 30%). This means that increase of the  $\text{Li}_2\text{O}$  concentration leads to decrease of the medium-range structure correlations; at concentration  $z\%$  the decrease of the characteristic length is roughly also  $z\%$  at least in the interval 5%–28%.

## B. Quasielastic scattering

At lowest frequencies of the measurements the quasielastic light scattering dominates the spectra, Fig. 1. QELS is seen in the frequency interval from  $0.06\omega_b$  up to  $\sim 0.3\omega_b$  (e.g., 4–25  $\text{cm}^{-1}$  for  $x=0.28$ ). To enhance the QELS part of the spectra, they are shown in the insert of Fig. 1 in the log  $\omega$  coordinate. Similar to the boson peak, QELS roughly scales on a universal curve for different compositions.

QELS arises due to a fast relaxation process with a relaxation time  $\tau$  on the order of a picosecond.<sup>1</sup> It was investigated in many glasses by means of the light and neutron scattering (see, e.g., Ref. 26 for a small review). Recently, broad band light scattering measurements by tandem Fabry-Perot interferometer<sup>17-20</sup> revealed a broad (1–100 GHz) low-frequency wing of the fast relaxation in glasses described by a power law with an exponent  $\alpha < 1$ . However, in the frequency region close to the boson peak the QELS spectrum normally was successfully fitted by a Lorentzian.<sup>15,16,27-30</sup> In the present paper we fitted the fast relaxation spectrum also by a Lorentzian which was defined by the two parameters: the width  $\tau^{-1}$  and the strength of the relaxation process,  $\delta^2$ , which is equal to the ratio of the integrals over the fitted QELS spectrum and that over the boson peak. The vibration spectrum we fitted by the power law  $I \propto \omega^\alpha$  extrapolated from

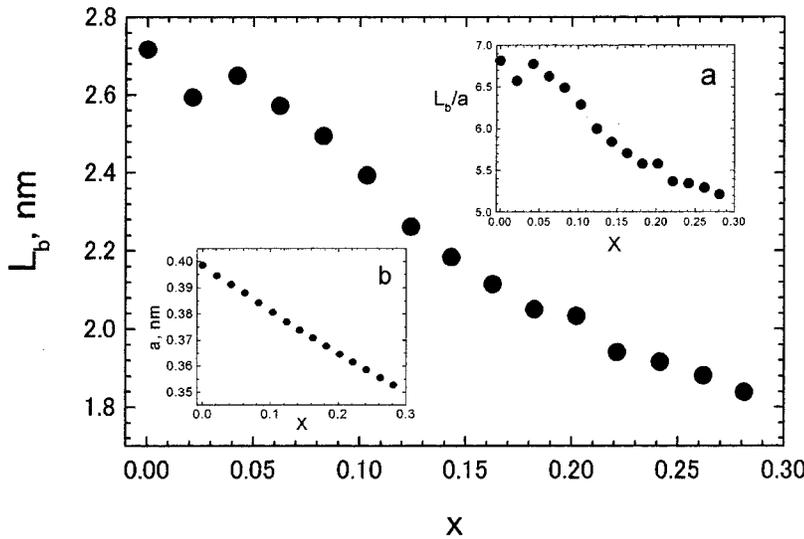


FIG. 6. Correlation length defined by Eq. (2). Insets: (a) the ratio of the correlation length  $L_b$  to the average interatomic distance  $a$ ; (b) the dependence of  $a$  on the composition.

the interval around  $0.5\omega_b$ . The fits coincide with the experimental curves within the experimental error. The master curve in Fig. 3 gives  $a=2$  with the slopes of the individual curves scattered around this value in  $\sim 10\%$  interval. Within the same error we found  $\delta^2 \approx 0.09$  in all samples except those with  $x \leq 0.04$ ; at these low concentrations no reliable estimation of the QELS parameters was available due to the finite low-frequency resolution of the experiment of about  $5 \text{ cm}^{-1}$ . The dependence of the parameters  $\tau^{-1}$  and  $\omega_b$  on the composition is shown in Fig. 2. As it is expected already from the fact that QELS for different compositions scales on the master curve together with the boson peak (Fig. 3), the width of QELS also scales with the boson peak frequency. Figure 7 shows that in rough approximation there is a linear correlation between  $\tau^{-1}$  and the boson peak frequency. In Fig. 8 the ratio  $\tau^{-1}/\omega_b$  is plotted as a function of Li<sub>2</sub>O fraction; this figure shows that roughly  $\tau^{-1} \approx 0.24\omega_b$ .

These findings support the anharmonic model of the fast relaxation.<sup>15,31</sup> Within the frame of this model the anharmonicity of the lattice leads to the fast vibrational relaxation. Qualitatively, this relaxation process occurs due to the cou-

pling of a vibration mode to the fluctuations of vibration occupation number  $n(\omega)$  (or to temperature at high enough  $T$ ). Since  $n(\omega)$  is determined by the squared amplitude of the vibrations, such coupling is provided in first approximation just by the third order anharmonic coefficient, or Grüneisen parameter  $\gamma$ . Such relaxation process gives rise to a self-energy term  $M_\Omega(\omega)$  in the vibration susceptibility  $\chi_\Omega(\omega)$ ; in a single time approximation it can be written as

$$M_\Omega(\omega) = \frac{\delta^2 \Omega^2}{1 - i\omega\tau}. \tag{3}$$

Here  $\Omega$  is the frequency of the vibration and the parameter  $\delta$  characterizes the strength of the relaxation process. The model<sup>15</sup> predicts that

$$\delta^2 = \frac{\gamma^2 T}{M v_t^2}, \tag{4}$$

where  $M$  is the molar mass. Finally, in the same single-time approximation the reduced QELS intensity,  $I_r^{\text{QELS}} = I^{\text{QELS}}/\omega(n(\omega) + 1)$ , is equal to

$$I_r^{\text{QELS}}(\omega) \approx \frac{2}{\pi} \frac{\delta^2 \tau}{1 + \omega^2 \tau^2} \int I_r^{\text{vib}}(\Omega) d\Omega, \tag{5}$$

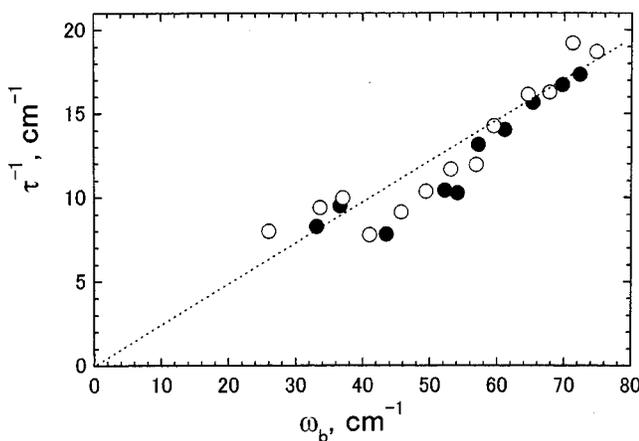


FIG. 7. Correlation between the inverse fast relaxation time  $\tau^{-1}$  (the width of the QELS line) and the boson peak frequency for a sequence of the lithium borate glasses of various composition. Solid circles, VV; open circles, VH polarization.

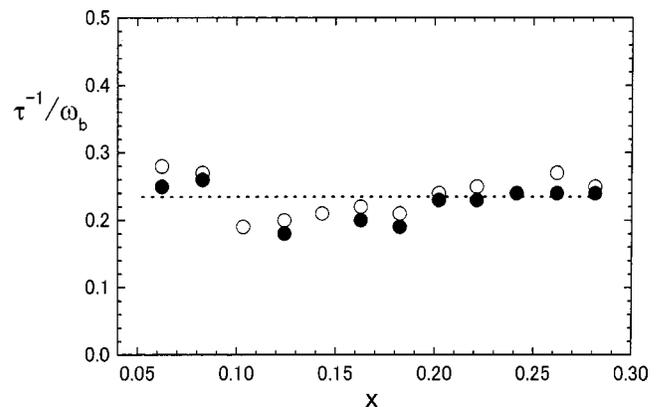


FIG. 8. The ratio of the width of QELS line to the boson peak frequency for data from Fig. 4. Solid circles, VV; open circles, VH polarization.

where  $I_r^{\text{vib}}(\Omega)$  is the reduced intensity of the light scattering by vibrations in the limit  $\delta=0$ .  $I_r^{\text{vib}}(\Omega)$  essentially represents the boson peak, so  $I_r^{\text{QELS}}(\omega)$  is proportional to the integral over the boson peak. Integrating over all  $\omega$ , Eq. (5) has

$$\delta^2 = \frac{\int I_r^{\text{QELS}}(\omega) d\Omega}{\int I_r^{\text{vib}}(\Omega) d\Omega}, \quad (6)$$

so, according to Eq. (4) the integral over the QELS spectrum gives information about the Grüneisen parameter.

The anharmonic model makes prediction that the width of the QELS spectrum correlates with the frequency of the boson peak, namely,

$$\tau^{-1} \approx \omega_b/3. \quad (7)$$

This relation is given by a simplified estimation, thus the coefficient between  $\tau^{-1}$  and  $\omega_b$  may be somewhat different from 1/3. There was a phenomenological observation<sup>15,31</sup> that in various glasses at  $T=T_g$  this relation holds surprisingly good. However, up to now there was no data on the relation between  $\tau^{-1}$  and  $\omega_b$  in a sequence of glasses with similar chemical composition in a broad range of  $\omega_b$  values. The lithium borate glasses give a rare case of the very strong shift of the boson peak as a function of a one smooth variable, composition  $x$ , making it possible to check the prediction of Eq. (7). As we have seen above, our data holds this relation with the coefficient 0.24 instead of 1/3. Although 1/3 is only a rough estimate, one should note that the fast relaxation time, as it is known from the analysis of the light scattering data in other glasses (e.g., Refs. 15, 16, and 27–30) normally weakly decreases when temperature increases; since we analyzed the room temperature data, one can expect at the glass transition  $\tau^{-1}$  will be a little bit higher. The data of Ref. 28 in supercooled  $\text{B}_2\text{O}_3$  indeed gives for  $\tau^{-1}$  the value  $\omega_b/3$  at  $T=T_g$ .<sup>15</sup>

### C. Anharmonicity

Using the value  $\delta^2 \approx 0.1$  obtained by fitting the QELS spectrum as described above, one can estimate the Grüneisen parameter  $\gamma$  for the boson peak within the anharmonic model of the fast relaxation Eq. (4). Taking the  $v_t$  and  $T_g$  data for our set of the lithium borate glasses from Ref. 25 (Fig. 4), we obtained  $\gamma$  shown in Fig. 9(a). Figure 9(a) shows that estimated from QELS data Grüneisen parameter increases from 4 to 6 in the interval  $x=0.06-0.28$ . This means that the anharmonicity of the boson peak vibrations in lithium borate glasses increases with an increase of the lithium oxide fraction.

For lithium borate glasses the temperature variations of the sound velocity and of the density are known.<sup>32</sup> Thus, one can determine the Grüneisen parameter  $\gamma_D = \partial \ln \omega_D / \partial \ln V$  for the Debye frequency defined by Eq. (1). If  $\alpha$  is a volume thermal expansion coefficient,  $\alpha = \partial \ln V / \partial T$  and  $k_l$ ,  $k_t$ , and  $k_D$  are the thermal coefficients for the longitudinal, transversal, and Debye velocities, respectively (e.g.,  $k_t = \partial \ln v_t / \partial T$ ), then

$$\gamma_D = 1/3 - k_D/\alpha, \quad (8)$$

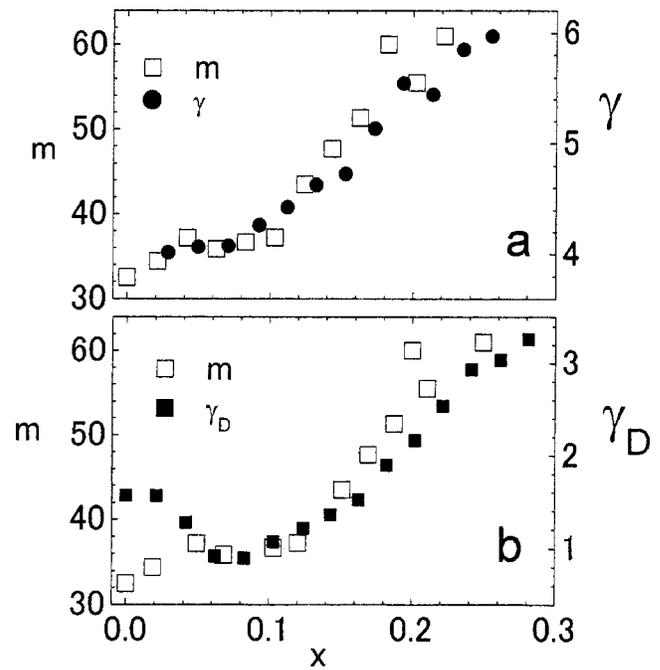


FIG. 9. Correlation between the Grüneisen parameters and fragility for glasses of different composition. (a) Grüneisen parameter for the Debye frequency  $\gamma_D$  (solid squares) and fragility  $m$  (open squares); (b) Grüneisen parameter for the boson peak  $\gamma$  (solid circles) and fragility. The data for fragility are taken from Ref. 23.

where

$$k_D = \frac{v_D^3}{3} \left( \frac{2k_t}{v_t^3} + \frac{k_l}{v_l^3} \right). \quad (9)$$

The parameter  $\gamma_D$  is shown in Fig. 9(b). Since the high-frequency vibrations near the end of the acoustical spectrum relax weaker than the boson peak vibrations,  $\gamma_D$  is less than the respective parameter  $\gamma$  for the vibrations in the region of the boson peak. However, the general behavior of  $\gamma_D$  and  $\gamma$  is similar except the region of low-concentration of  $\text{Li}_2\text{O}$ , where we have no data for  $\gamma$ .

An important property of glassformers is the so-called fragility which shows how quickly the viscosity  $\eta$ , or  $\alpha$ -relaxation time, changes in the glass transition region if temperature is scaled by  $T_g$ .<sup>33</sup> The nature of the fragility is still not fully understood. In Ref. 24 it was noted that the intensity of the QELS in glassformers, normalized to that of the boson peak at  $T=T_g$ , correlates with the fragility. The anharmonic model of the fast relaxation predicts that the intensity of QELS in a glass is determined by the cubic anharmonic coefficient, so in Ref. 15 it was claimed that the fragility increases together with anharmonicity. This was checked and confirmed in Ref. 15 for a few different glassformers. Here we have a possibility to check the correlation for a sequence of glassformers of similar composition. The latter makes unimportant such factors as different types of chemical bonding and structure which may influence the comparison in the case of different materials.

The fragility is quantified by the parameter  $m$  defined as

$$m = \frac{d \ln \eta}{dT_g/T} \text{ at } T \rightarrow T_g. \quad (10)$$

We took the data for the fragility of lithium borate glasses for some  $x$  in the literature.<sup>23</sup> In Fig. 9 the dependence of the parameter  $m$  on the composition is compared with that of the Grüneisen parameters. One can see that indeed there is a correlation of the fragility with the Grüneisen parameters; the higher anharmonicity corresponds to higher fragility.

In Ref. 34 a correlation between the fragility and the correlation length was discussed. It was found that in different materials the correlation length has a tendency to decrease with increasing fragility of the glassformer. Such comparison of course has more sense in a series of samples of a similar chemical composition. We note that indeed, in the case of lithium borate glasses fragility increases while the correlation length decreases with increasing the  $\text{Li}_2\text{O}$  fraction (Figs. 6 and 9), except the region  $x < 0.08$  where the behavior is more complicated. This corresponds to the ideas that fragility is higher in more structurally (but not chemically) homogeneous glasses and decreases with increase of the structure heterogeneity on the nanometer scale.<sup>35</sup>

The structural basis for changing of the fragility in lithium borate glasses is not clear. The increase of the fragility in lithium borate glasses with  $x$  is in agreement with the model of Vilgis<sup>36</sup> in which the degree of fragility is connected to the fluctuations of the coordination number in the system,  $\Delta z$ . Network glasses with fixed covalent bonding have  $\Delta z = 0$ , and, respectively, they are strong glassformers. Fragile systems always have nonzero  $\Delta z$ . In pure boron oxide the boron atom has a fixed valence equal to 3. Possible small fluctuations of the number of covalent bonds are connected only to the structure defects. In the case of lithium borate glasses some boron atoms have valence 4 in the structural units  $\text{Li}^+\text{BO}_4^-$ . Thus, the number of the covalent bonds of boron atoms fluctuates between 3 and 4. A NMR study of Jellison *et al.*<sup>37</sup> showed that the fraction of 4-coordinated boron atoms,  $p_4$ , for  $0 \leq x \leq 0.28$  is determined by  $x$  as follows:  $p_4 = x/(1-x)$ . The average number of valence bonds per boron atom is  $\bar{z} = 4p_4 + 3(1-p_4) = 3 + x/(1-x)$ . It is easy to find the squared fluctuation of  $z$ ,  $\overline{\Delta z^2} = \overline{z^2} - \bar{z}^2 = p_4(1-p_4)$ . One has  $\overline{\Delta z^2} = x(1-2x)/(1-x)^2 \approx x + O(x^3)$ . Thus, neglecting the third power term of the small parameter  $x$ , we see that the correlation between the fragility  $m$  and  $\overline{\Delta z^2}$  means that there should be also the same correlation between  $m$  and  $x$  in Fig. 9. Thus, at least in the case of the lithium borate glasses fragility indeed correlates with the degree of fluctuations of the boron coordination number.

Differential thermal analysis (DTA) of the lithium borate glasses in the vicinity of the glass transition<sup>25</sup> reveals the onset temperature  $T_g$ , the peak temperature  $T_p$ , and the end temperature  $T_e$  in terms of the phenomenological theory of the glass transition.<sup>38</sup> The former temperature is often referred to as the glass transition temperature. Figure 10 shows schematically a part of the DTA heating curve in the vicinity of the glass transition with the definition of the three temperatures. In DTA, the temperature difference is measured between the sample to be studied and the standard sample. So, in Fig. 10,  $\Delta T$  is the difference of temperatures between the sample to be studied and the standard sample in the DTA setup. The details of the measurements are described in Ref.

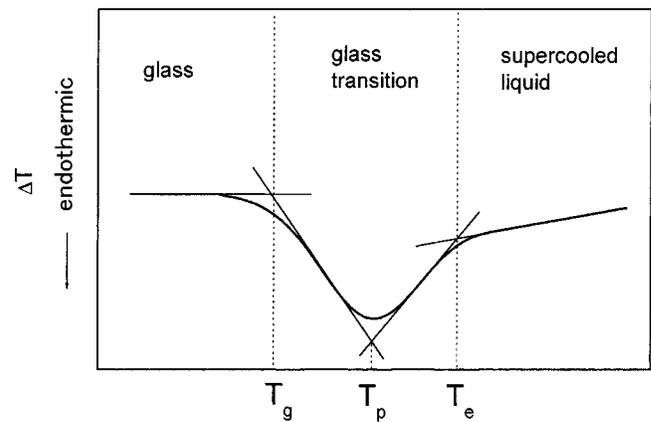


FIG. 10. Schematic differential thermal analysis curve of the glass transition.

25. Here we compare the width of the glass transition region which we define as  $\Delta T_g = T_e - T_g$  with the anharmonic properties and fragility. We are motivated by the results of the analysis of the glass transition in terms of the mode coupling theory.<sup>39</sup> The theory predicts the so-called critical temperature  $T_c$  of the ideal glass transition; it was found that  $T_c > T_g$ . Phenomenological analysis has shown that the relative interval  $(T_c - T_g)/T_g$  is larger in strong glassformers and lesser in the fragile.<sup>26,35,40</sup> Here we check if such correlation exist also between the width of the glass transition, fragility, and anharmonicity. In Fig. 11, both  $T_g/\Delta T_g$  and the Grüneisen parameter for the Debye frequency are shown as a function of the composition. The correlation of the relative width of the glass transition with the anharmonic parameter is very good even at low  $x < 0.1$ . The parameters  $\gamma$  and  $m$  correlates with  $T_g/\Delta T_g$  as good as  $\gamma_D$ ; we show only the latter since it was determined in a broader interval of  $x$ . These results show that at least in a series of lithium borate glasses with different composition the normalized width of the glass transition strongly correlates with the fragility and anharmonicity of the samples; this stresses the importance of the anharmonic effects for the theory of the glass transition.

#### IV. CONCLUSION

Due to a strong dependence of the boson peak frequency on the composition the lithium borate glasses give an excellent opportunity to investigate correlations between the low-frequency Raman spectra (quasielastic scattering and the boson peak), anharmonicity, and fragility. We fitted the quasielastic line by a single relaxation time function and using this data and the anharmonic model of the fast relaxation<sup>15</sup> found the Grüneisen parameter for the boson peak vibrations. We estimated also the Grüneisen parameter for the Debye frequency and found out that both parameters increase when  $\text{Li}_2\text{O}$  fraction increases. Comparison of the anharmonicity parameters with the fragility in the samples of the same composition showed that they strongly correlate; higher anharmonicity corresponds to higher fragility. In a good agreement with the predictions of the anharmonic model<sup>15</sup> the width of the quasielastic line is proportional to the boson peak frequency. We found a characteristic—

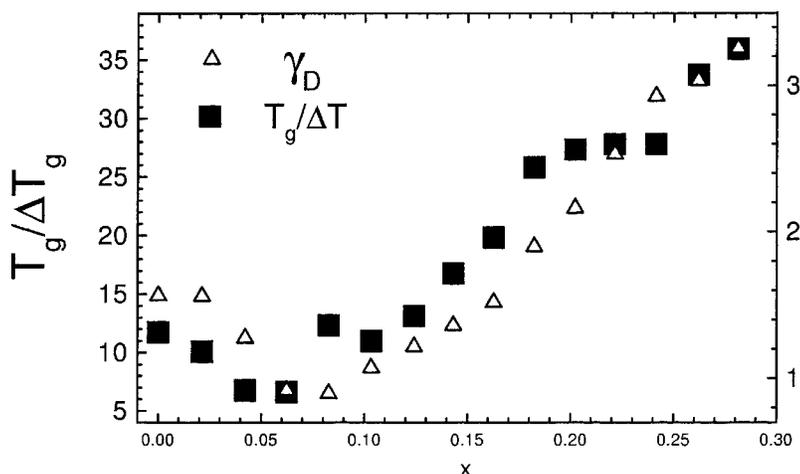


FIG. 11. Correlation of the width of the glass transition region,  $T_g/\Delta T_g$  with the Grüneisen parameter  $\gamma_D$ .

medium range length  $L_b$  of the boson peak vibrations decreases with increasing fraction of  $\text{Li}_2\text{O}$  not only in absolute units, but also if measured in respective interatomic distances; this confirms an assumption that increase of fragility corresponds to decrease of the structure correlation length.<sup>23</sup> It is shown that the width of the glass transition region in the series of lithium borate glasses depends on the composition like the Grüneisen parameters. Thus, the anharmonic properties of the material correlates both with the fast relaxation and with the primary one. For the former it determines the strength of the relaxation process and for the latter, such parameters, such as, fragility and the width of the glass transition region.

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