PHYSICAL REVIEW B **78**, 024104 (2008)

Thermally activated relaxations and vibrational anharmonicity in alkali-borate glasses: Brillouin scattering study

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(Received 7 November 2007; published 10 July 2008)

Measurements of Brillouin light scattering have been performed in $(M_2O)_{0.14}(B_2O_3)_{0.86}$ alkali-borate glasses, where M=Li and K, as a function of temperature between 15 and 300 K. The temperature behaviors of hypersonic attenuation and velocity have been explained in terms of thermally activated relaxations of intrinsic structural defects and of anharmonic interactions between hypersonic waves and thermal vibrational modes. In the temperature region above 150 K, where the mean free path of thermal modes is shorter than the acoustic wavelength, it has been shown that the sound propagation is mainly regulated by the Akhiezer mechanism of "phonon viscosity." It causes a linear increase in the hypersonic attenuation and a linear decrease in the sound velocity with increasing temperature.

DOI: 10.1103/PhysRevB.78.024104 PACS number(s): 61.43.Fs, 62.40.+i, 62.80.+f

I. INTRODUCTION

In the study of acoustic properties of glasses, considerable effort is currently expended to understand the mechanisms driving the temperature behaviors observed in the gigahertz frequency range.[1–4] In the kilohertz and megahertz ranges, in fact, the acoustic behaviors of oxide glasses are mainly regulated by local motions of structural defects, that is, by tunneling at low temperatures ($T<20$ K) and classical activation at higher temperatures ($T>20$ K).[5–8] They cause: (i) an increase in the acoustic attenuation (or equivalently the internal friction Q^{-1}) at the lowest temperatures followed by a temperature-independent plateau and then by a well pronounced peak and (ii) the associated variations in the sound velocity. At variance with these observations, the hypersonic internal friction between a few kelvins and the glass transition temperature T_g exhibits features which point to the presence of an excess contribution over that provided by thermally activated relaxation processes. Silica glasses with different OH contents show an attenuation peak, centered at about 150 K, followed by a plateau range, where the internal friction remains high and weakly temperature dependent up to T_g.[9] Quite differently, glassy B_2O_3 and a multicomponent glass reveal an increasing internal friction with increasing temperature up to about 100 K followed by a T-independent plateau up to T_g.[3] Contradictory interpretations have been offered to explain the behavior revealed in glassy SiO_2. The first one assumes the existence of defect states, schematized by asymmetric double-well potentials, experiencing thermally activated jumps between different configurations. At least qualitatively, it was able to describe the temperature variations in the internal friction over the frequency range from kilohertz to gigahertz in glassy SiO_2 (Ref. 10) and GeO_2.[11] More recently, an accurate analysis of the results obtained in glassy SiO_2 and in permanently densified glassy SiO_2 (Ref. 2) proved that the anharmonic interactions between longitudinal-acoustic waves and thermal phonons contribute substantially to the hypersonic attenuation in the region of temperatures above the attenuation peak. In both of the analyses cited above, it was impossible to use the behavior of the sound velocity as a convincing support for the influence of the vibrational anharmonicity in the temperature region above the peak. Tetrahedrally coordinated glasses (such as SiO_2, GeO_2, and BeF_2), in fact, show an anomalous hardening with increasing temperature, which leads to a positive temperature coefficient of the sound velocity, in clear contrast with the linear decrease in the elastic constants provided by vibrational anharmonicity.[12,13]

Very recently, studies concerning the sound propagation in alkali- and silver-borate glasses[7,8] showed that classical activation of defect states regulates the sound velocity between 20 and 120 K, whereas the vibrational anharmonicity becomes dominant at even higher temperatures. It has been also observed that the latter mechanism gives a negligible contribution to the internal friction in the ultrasonic range. Since the contribution of vibrational anharmonicity to the attenuation is expected to increase strongly with increasing frequency, becoming relevant in the gigahertz range,[14] the hypersonic attenuation and sound velocity have been measured by Brillouin light scattering (BLS) in alkali-borate glasses $(M_2O)_{0.14}(B_2O_3)_{0.86}$ with the same composition but different cations with increasing sizes from M=Li to M=K. This specific composition has been selected in order to avoid the formation of nonbridging oxygens in the glassy network,[8] which could cause undesired contributions to the acoustic behaviors. The experimental results show that with increasing temperature above about 50–60 K, vibrational anharmonicity gives a significant contribution to the hypersonic attenuation of these borate glasses over that provided by thermally activated relaxations of defect states.

II. EXPERIMENTAL DETAILS

$(M_2O)_{0.14}(B_2O_3)_{0.86}$ alkali-borate glasses, with M=Li and K, were prepared and characterized following the same specific procedures already described.[7,8] In the following the acronyms LiBO and KBO will be used to indicate lithium- and potassium-borate glasses, respectively.

BLS experiments were performed in a near backscattering geometry with a Sandercock tandem-multipass (3+3 passes) interferometer in order to determine the attenuation and the velocity of longitudinal sound waves. The light source was an Ar^+ laser operating at 514.5 nm. The Fabry-Pérot interferometer was equipped with a standard flow cryostat using liquid helium or nitrogen for thermal scanning between 15 and 300 K. Brillouin lines with shifts $\upsilon_B \sim 30.6$ GHz (LiBO) and $\upsilon_B \sim 25.3$ GHz (KBO) were analyzed by a fitting procedure involving a Lorentzian function $[\Gamma/2\pi$ is the half-width at half maximum (HWHM)] convoluted with a resolution function experimentally determined. The internal friction Q^{-1} is determined by the ratio between the full width at half maximum and the shift υ_B of the Brillouin line: $Q^{-1} = 2\Gamma/2\pi\upsilon_B$. The hypersonic sound velocity V is obtained by using the shift υ_B and the index of refraction n of the studied materials: $\upsilon_B = 2nV/\lambda_0 \sin\theta/2$, where λ_0 is the wavelength of the incident light and θ is the scattering angle. The room-temperature values of the indices of refraction, interpolated from the curves obtained in alkaline borate glasses at a wavelength of 514.5 nm by Lorosch *et al.*[15] have been used for the whole temperature range studied, leading to systematic errors in the determination of the sound velocity. The values of sound velocity at 300 K are little higher (few percent) than those measured in the megahertz range, which are shown in parentheses for comparison: $V_l = 5236$ m s^{-1} (5060 m s^{-1}, at 10 MHz) for LiBO and $V_l = 4376$ m s^{-1} (4221 m s^{-1}, at 10 MHz) for KBO.

The specific-heat capacities of the samples were determined between 120 and 350 K using a PerkinElmer differential scanning calorimeter (DSC) and the software PYRIS. Disks of each glass with a mass of approximately 15 mg were encapsulated in aluminum pans and subjected to a heating run at 20 K/min. Calibrations of the DSC output were performed using a standard sapphire sample. In the temperature range explored, the specific heats of all the studied systems varied smoothly with increasing temperature from 0.28 J(g K)$^{-1}$ at 120 K up to 0.98 J(g K)$^{-1}$ at 350 K in LiBO and from 0.27 J(g K)$^{-1}$ at 120 K up to 0.91 J(g K)$^{-1}$ at 350 K in KBO.

III. RESULTS

The temperature dependences of Brillouin linewidths for $(M_2O)_{0.14}(B_2O_3)_{0.86}$ glasses in the region from 15 to 300 K are reported in Fig. 1(a). To compare the hypersonic data with those previously obtained on the same samples in the ultrasonic range,[8] the experimental results have been transformed into the internal friction $Q^{-1} = 2\Gamma/2\pi\upsilon_B = \alpha V/\omega$, where α is the ultrasonic energy attenuation, V is the sound velocity, and ω is the ultrasonic angular frequency. These results are reported in Fig. 1(b). In LiBO, the internal friction increases with increasing temperature toward a broad peak, centered at about 105 K; at even high temperatures it decreases just a little, exhibiting a nearly constant value up to 300 K. The loss peak becomes less evident and shifts to higher temperatures with increasing cation size from Li to K.

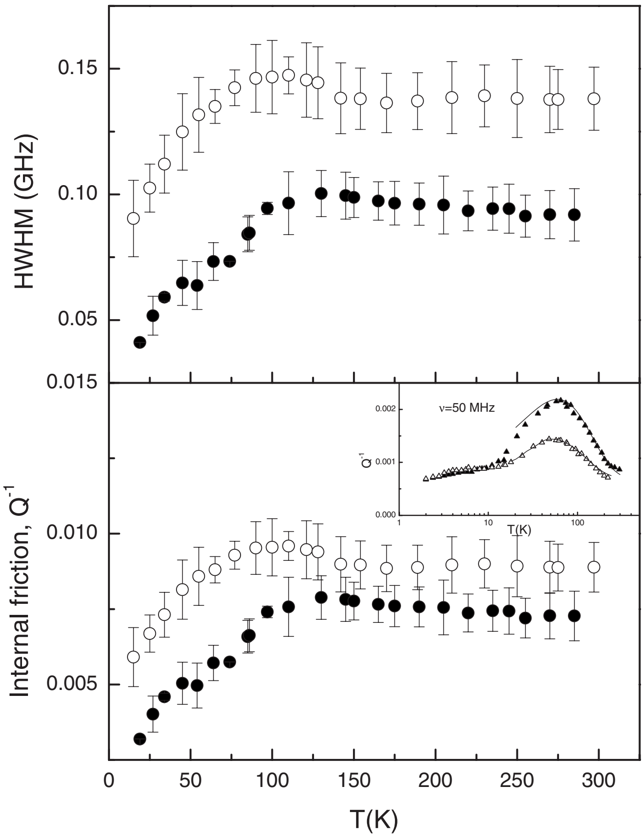

FIG. 1. (a) The temperature dependence of the HWHM in $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ (○) and $(K_2O)_{0.14}(B_2O_3)_{0.86}$ (●) glasses. (b) The temperature dependence of the internal friction Q^{-1} at hypersonic frequencies in $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ (○) and $(K_2O)_{0.14}(B_2O_3)_{0.86}$ (●) glasses. The inset shows the comparison between the experimental data of Q^{-1} measured at 50 MHz in the same glasses: LiBO (Δ) and KBO (▲); the solid lines represent the relaxation loss evaluated by using Eq. (4).

The temperature dependence of Brillouin shift in LiBO, reported in Fig. 2(a), is typical. The fractional variations in longitudinal sound velocity, $\delta V_l = V_l(T) - V_{l,0}$, with $V_{l,0}$ as the sound velocity at the lowest temperature in the experiment, have been determined for both the borate glasses by using the frequency shift υ_B and are compared in Fig. 2(b). As already observed in the megahertz range,[7,8] the sound velocity decreases with increasing temperature in the whole investigated range but exhibits a larger slope at low temperatures and a nearly linear trend at higher temperatures. These behaviors mirror the ultrasonic ones, which have been explained by considering a low-temperature relaxation process overlapping with the vibrational anharmonicity of the glassy network.[7,8]

Figure 1(b) shows that the experimental data of hypersonic internal friction, evaluated by using the HWHM of Brillouin lines, do not decrease sufficiently fast with decreasing temperature, pointing to a finite value at 0 K. This feature, particularly evident in LiBO, is a clear indication of an additional contribution to the dynamic sound attenuation which arises from small density fluctuations within the scattering volume. Despite the careful procedure used to obtain homogeneous and well stabilized glasses,[7] submicrohetero-

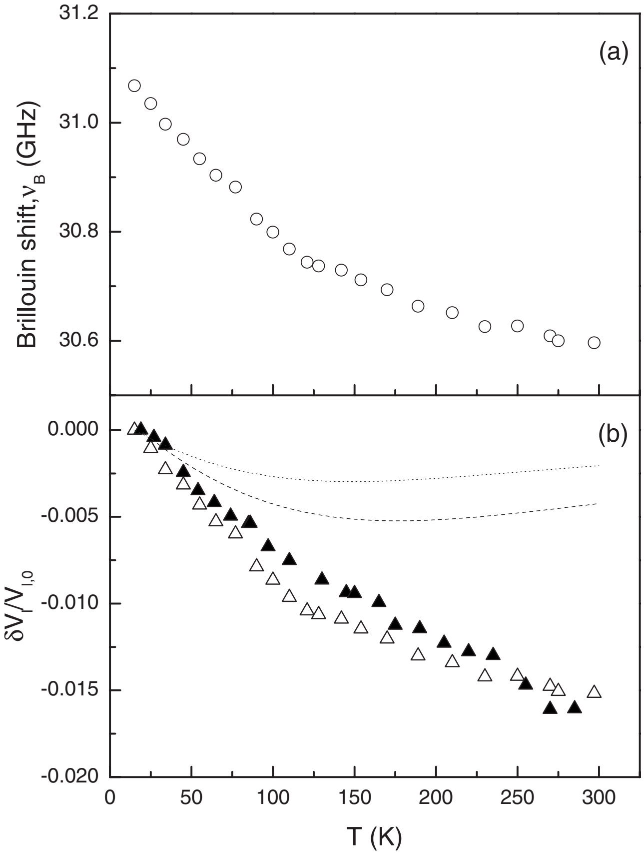

FIG. 2. (a) The temperature dependence of the Brillouin shift ν_B in $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ glass. (b) Temperature dependence of the fractional sound velocity $\delta V_l(T)/V_{l,0}$ of hypersonic longitudinal waves in $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ (Δ) and $(K_2O)_{0.14}(B_2O_3)_{0.86}$ (▲) glasses. The dotted (LiBO) and dashed (KBO) lines represent the relaxation contributions to the sound velocity evaluated at hypersonic frequencies by using Eq. (5).

geneous regions are expected in two-component alkali-borate glasses.[16] They cause small inhomogeneities in the local density and a consequent broadening of Brillouin lines,[17] which can be assumed as temperature independent in the glassy phase. Probing different regions of the samples, symmetric Brillouin lines with small differences in υ_B and in the linewidths have been observed; the experimental data reported here refer to the narrowest lines, which mark the most homogeneous regions of these borate glasses. The evaluation of the attenuation background due to static inhomogeneities has been performed by considering the results of a recent ultrasonic study on the same glasses over the temperature interval between 1 and 300 K.[8]

The internal friction of 50 MHz ultrasonic waves [inset of Fig. 1(b)] rises with increasing temperature until it reaches a plateau followed by a broad loss peak, which arises from thermally activated relaxations of structural defects.[8] The plateau is determined by the interaction of acoustic waves and two-level or tunneling systems (TLS), which experience a relaxation assisted by phonons. This mechanism, characteristic of glasses and some disordered crystals,[6] was theoretically explained by Jackle[18] within the framework of the standard tunneling model. It provides for a temperature-independent internal friction, determined only by the so-called tunneling strength C: $Q^{-1}_{\mathrm{plateau},i}=(\pi/2)[\bar{P}\gamma_i^2/\rho V_i^2]=(\pi/2)C_i$. Here C_i is the tunneling strength, υ_i is the ultrasonic wave velocity, γ_i is the deformation potential that expresses the coupling between the ultrasonic stress and the system, $\bar{P}$ is the TLS spectral density, ρ is the sample density, and the index i refers to the different polarizations (longitudinal or transverse). The plateau extends over a temperature interval limited by two characteristic temperatures $\tilde{T}$ and T^*, which mark distinct three temperature regions:[5] (i) very low temperatures ($T<\tilde{T}$), $Q^{-1}\propto T^3$; (ii) the plateau region ($\tilde{T}<T<T^*$), Q^{-1} is temperature independent; and (iii) $T>T^*$, $Q^{-1}\propto T$ up to a temperature $T_{\max}$, at which an internal friction maximum occurs, resulting in a decrease at even higher temperatures ($Q^{-1}\propto T^{-1}$ for $T>T_{\max}$). It is worth noting that for $T>T^*$, the TLS dynamics changes drastically, experiencing incoherent tunneling motion within the two potential wells schematizing a TLS. Moreover, if the same defect states give rise to tunneling motion at low temperatures and classical activation at higher temperatures, thermal activation will exceed the tunneling rate with increasing temperature above about 20 K, becoming the dominant mechanism.[5] The temperatures $\tilde{T}$ and T^* are regulated by different frequency behaviors: $\tilde{T}$ increases proportionally to $\omega^{1/3}$, while T^* is frequency independent and marks the end of the plateau. As a consequence of above, $\tilde{T}$ grows significantly with increasing frequency, approaching T^* and reducing the plateau to a shoulder of the attenuation peak at frequencies close to 1 GHz.[19]

It should be also noted that the magnitude of the plateau could be slightly frequency dependent, a circumstance which leads to frequency-dependent values of C. The comparison of $Q^{-1}_{\mathrm{plateau}}$ in glassy SiO_2 for frequencies spanning 5 orders of magnitude gives a difference of about a factor of 2.[6] In vitreous B_2O_3, however, the same comparison performed over about 4 orders of magnitude in frequency gives very close values: $Q^{-1}_{\mathrm{plateau}}=6\times10^{-4}$ at 2.8 kHz (flexural waves; Ref. 5) and $Q^{-1}_{\mathrm{plateau}}=7.2\times10^{-4}$ at 20 MHz (longitudinal waves; Ref. 20). The preceding results, obtained by comparing data from *different* types of experiments, lead us to consider Jackle's theory as *fully valid* and to assume the values of C_l determined by the plateau observed at ultrasonic frequencies in these borate glasses as a reference for the evaluation of the background due to static inhomogeneities in the hypersonic range.

The temperature T^* has been directly determined by the experimental curves [inset of Fig. 1(b)], giving the following values: $T^*\sim11$ K in LiBO and $T^*\sim9$ K in KBO. Since in the temperature region $T^*<T<T_{\max}$ the internal friction is regulated by incoherent tunneling of TLS and is given by $Q^{-1}_{\mathrm{TS},l}=(\pi^2/8)C_l(T/T^*)$,[5] it has been possible to evaluate the values of $Q^{-1}_{\mathrm{TS},l}$ at the lowest temperatures in the experiment by the values of T^* and of C_l determined at ultrasonic frequencies.[8] The obtained values, used as a reference for estimating the inhomogeneous background Q^{-1}_{back}, are $Q^{-1}_{\mathrm{TS},l}(15\ \mathrm{K})=0.0011$ for LiBO and $Q^{-1}_{\mathrm{TS},l}(19\ \mathrm{K})=0.0013$ for KBO. The attenuation background, given by $Q^{-1}_{\mathrm{back}}=Q^{-1}_{\mathrm{exp}}-Q^{-1}_{\mathrm{TS}}$, has been determined at 15 K for LiBO and at 19 K for

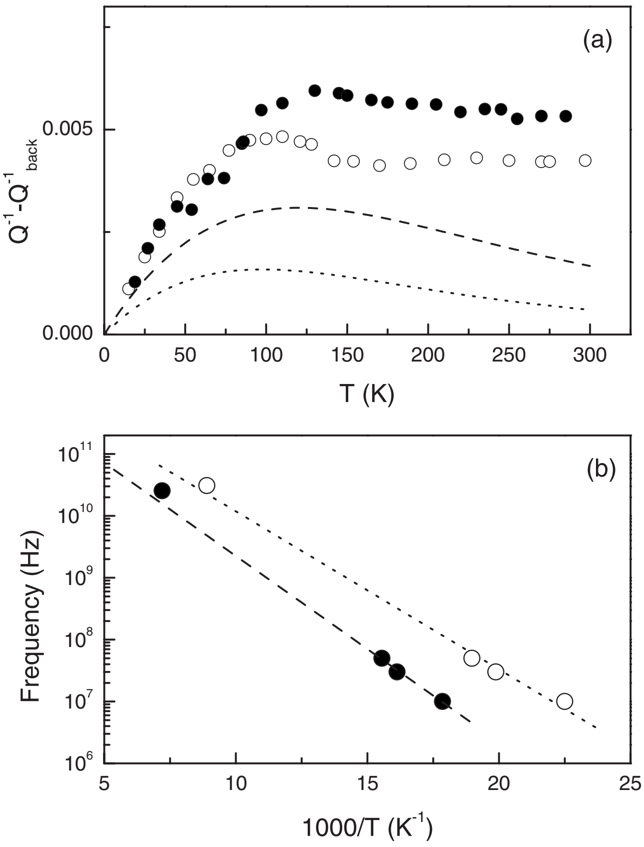

FIG. 3. (a) Temperature dependence of the experimental internal friction after subtraction of the background contribution Q^{-1}_{back} due to static inhomogeneities (see text). The dotted (LiBO) and dashed (KBO) lines represent the relaxation contributions $Q^{-1}_{\mathrm{rel,hyper}}(T)$ to the internal friction evaluated at hypersonic frequencies by using Eq. (4). (b) Arrhenius plot of the loss peaks of $(\mathrm{Li_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (○) and $(\mathrm{K_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (●) glasses. The dotted (LiBO) and dashed (KBO) lines represent the Arrhenius curves determined by the values of the average activation energy E_{act} and the characteristic frequency τ_0^{-1} obtained in the megahertz range.

KBO, obtaining the following values: $Q^{-1}_{\mathrm{back}}(15\ \mathrm{K})=0.0048$ for LiBO and $Q^{-1}_{\mathrm{back}}(19\ \mathrm{K})=0.0019$ for KBO. The Q^{-1}_{back} values are quite large; they are as high as 53% and 26% of the value of the high-temperature internal friction ($T>100$ K) for LiBO and KBO, respectively. Even if the background attenuation arises from static inhomogeneities and, consequently, is temperature independent, large values of Q^{-1}_{back} can significantly affect any kind of quantitative evaluation. Therefore the following analysis will have the main aim of showing that, in addition to the static contribution, the hypersound attenuation is determined by the two dynamic mechanisms arising from thermally activated relaxations and vibrational anharmonicity.

The curves for $Q^{-1}_{\mathrm{exp}}-Q^{-1}_{\mathrm{back}}$, obtained by subtracting Q^{-1}_{back} from the experimental internal friction, are reported in Fig. 3(a) and show that the internal friction maximum increases and shifts to higher temperatures by going from LiBO to KBO, as observed in the megahertz range [inset of Fig. 1(b)]. For both LiBO and KBO glasses, the internal friction peak is clearly visible. The peak temperature T_{peak} at hypersonic frequencies well fits the Arrhenius plot [Fig. 3(b)] determined by the values of the average activation energy E_{act} and the characteristic frequency τ_0^{-1} obtained in the megahertz range:[8] $E_{\mathrm{act}}/k_B=587$ K and $\tau_0^{-1}=2.23\times10^{13}$ s^{-1} for LiBO and $E_{\mathrm{act}}/k_B=683$ K and $\tau_0^{-1}=1.24\times10^{13}$ s^{-1} for KBO. This observation implies that a substantial contribution to the hypersonic Q^{-1} is given by the thermally activated relaxations which dominate the ultrasonic attenuation in the temperature range above 20 K.

IV. DISCUSSION

Following the above indications, the hypersonic internal friction and sound velocity have been first analyzed by considering the asymmetric double-well potential (ADWP) model, which schematizes the defect states by asymmetric double-well potentials with a barrier height V and an asymmetry Δ.[21] For temperatures higher than about 20 K,[5] a fraction of "particles" (single atoms or group of atoms) locally mobile within the glassy network experience thermally activated jumps between the two wells, which have barrier heights and asymmetries randomly distributed over the defect sites. A longitudinal sound wave of angular frequency ω propagating through the solid modulates Δ, giving rise to a relaxation process through the population of defects which causes an internal friction and a sound velocity variation given by[21,22]

$$Q^{-1}_{\mathrm{rel}}=\frac{\gamma_l^2}{\rho V_l^2 k_B T}\int\int d\Delta dV f(\Delta)g(V)\mathrm{sech}^2\left(\frac{\Delta}{2k_BT}\right)\frac{\omega\tau}{1+\omega^2\tau^2}, \tag{1}$$

$$\left(\frac{\delta V_l}{V_{l,0}}\right)_{\mathrm{rel}}=-\frac{\gamma_l^2}{2\rho V_l^2 k_B T}\int\int d\Delta dV f(\Delta)g(V)\times\mathrm{sech}^2\left(\frac{\Delta}{2k_BT}\right)\frac{1}{1+\omega^2\tau^2}. \tag{2}$$

In Eqs. (1) and (2), $f(\Delta)$ and $g(V)$ are the distributions of the asymmetries Δ and the barrier heights V and τ is the relaxation time given by

$$\tau=\tau_0\exp\left(\frac{V}{k_BT}\right)\mathrm{sech}\left(\frac{\Delta}{2k_BT}\right), \tag{3}$$

where the characteristic frequency τ_0^{-1} has been assumed to be single valued. Using an exponential form for $g(V)$, a constant value f_0 for $f(\Delta)$, and some simplifying assumptions, Gilroy and Phillips[22] (GP) derived analytical expressions which describe the behaviors of both Q^{-1}_{rel} and $(\delta V_l/V_{l,0})_{\mathrm{rel}}$ within a few percent error but over restricted intervals of temperature and frequency. More accurate expressions were proposed by Bonnet,[23] who extended the GP scheme to a wider range of temperature and frequency. By also including a Gaussian distribution with a width parameter Δ_G for the asymmetries, the following expressions which account for the temperature dependences of the acoustic loss and the sound velocity with a negligible error in the megahertz and gigahertz ranges have been obtained:[23]

$$Q^{-1}_{\mathrm{rel}}=C^*\left[\frac{\alpha\pi/2}{\cos(\alpha\pi/2)}y_0^{\alpha}-\frac{\alpha}{1-\alpha}y_0\right]\frac{\Phi(2\beta)}{\alpha}, \tag{4}$$

$$\left(\frac{\delta V_l}{V_{l,0}}\right)_{\mathrm{rel}} = \frac{C^*}{2}\left[\frac{\alpha\pi/2}{\sin(\alpha\pi/2)}y_0^{\alpha} - 1\right]\frac{\Phi(2\beta)}{\alpha}, \tag{5}$$

where $C^* = \gamma_l^2 f_0/\rho V_l^2$, $\alpha = k_B T/V_0 = T/T_0$, $\beta = k_B T/\Delta_G$, $y_0 = \omega\tau_0$, and $\Phi(2\beta)$ is the erf function. In the calculations, the relaxation time τ of the process has been approximated by the usual Arrhenius law, $\tau = \tau_0 e^{V_0/k_B T}$, where the average activation energy is the parameter V_0 of the distribution $g(V)$ given by the exponential form $g(V) = 1/V_0 \exp(-V/V_0)$.

Numerical evaluation of the ultrasonic relaxation loss (for $T \geq 20$ K) has been performed using the values of activation energy and characteristic frequency obtained by the Arrhenius plot ($T_0 = 587$ K and $\tau_0 = 4.48 \times 10^{-14}$ s for LiBO; $T_0 = 683$ K and $\tau_0 = 8.06 \times 10^{-14}$ s for KBO) as fixed parameters. A good fit of the experimental curves [solid lines in the inset of Fig. 1(b)] has been obtained with the following values for the remaining relaxation parameters: $C^{\times} = (3.3 \pm 0.14)^{\times} 10^{-3}$ and $\Delta_G/k_B = 295 \pm 15$ K for LiBO; $C^{\times} = (6.1 \pm 0.16)^{\times} 10^{-3}$ and $\Delta_G/k_B = 340 \pm 11$ K for KBO. Now that the relaxation parameters have been determined, it is possible to evaluate the relaxation loss at hypersonic frequencies by using the above values in Eq. (4). The resulting curves for $Q^{-1}_{\mathrm{rel,hyper}}(T)$ have been included in Fig. 3(a) as dotted (LiBO) and dashed (KBO) lines. The comparison between $Q^{-1}_{\mathrm{rel,hyper}}(T)$ and the experimental values of $Q^{-1}_{\mathrm{exp}} - Q^{-1}_{\mathrm{back}}$ reveals reasonable agreement between the peak temperatures, but it emphasizes that there is a considerable excess of hypersonic attenuation over that due to the relaxation process. The additional contribution, determined by subtracting $Q^{-1}_{\mathrm{rel,hyper}}(T)$ from the experimental curves, has been labeled as Q^{-1}_{anh} and is reported for the studied glasses in Fig. 4(a). As the temperature is increased from about 20 K, Q^{-1}_{anh} rises markedly until it reaches a region characterized by a much smaller slope which extends from about 120 up to 300 K. The additional source for this excess attenuation can be found by considering the temperature dependence of the sound velocity (Fig. 2), which reflects very closely those revealed in the megahertz range.[7,8] It has been clearly proved that the ultrasonic sound velocity in alkali-borate glasses is regulated by classical activation between 20 and 120 K and by the vibrational anharmonicity for even higher temperatures. Of course, anharmonicity also causes attenuation of sound waves, but its contribution is negligible in the megahertz range and is masked from the large high-temperature tail of the relaxation peak. Quite differently, the dispersion associated with a relaxation process is usually quite weak, allowing the unequivocal observation of the anharmonic contribution to the sound velocity. With increasing frequency from megahertz to gigahertz, the interactions between sound waves and thermal vibrations become a more efficient source of sound attenuation as observed in a number of crystalline oxides where temperature behaviors mirroring those reported in Fig. 4(a) have been revealed.[14,24] The damping of hypersounds in glasses due to anharmonicity was quantitatively investigated by Vacher *et al.*[2] and Rat *et al.*[17] They analyzed the hypersonic loss in vitreous silica over a wide temperature range and concluded that the anharmonic interactions between longitudinal-acoustic waves and the thermal bath contribute substantially to the hypersonic attenuation.

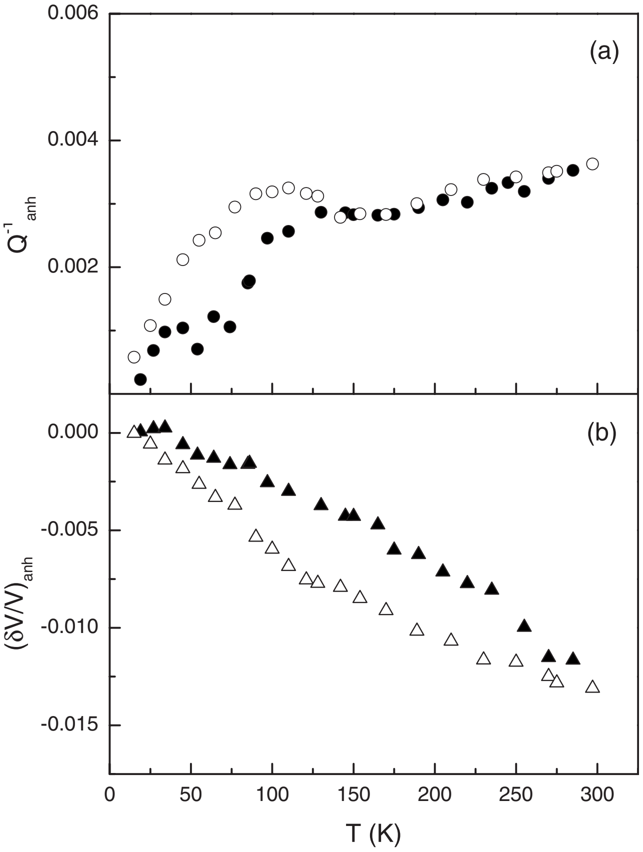

FIG. 4. (a) Temperature dependence of the anharmonic contribution to the internal friction, Q^{-1}_{anh}, for $(\mathrm{Li_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (○) and $(\mathrm{K_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (●) glasses. (b) Temperature dependence of the anharmonic contribution to the fractional sound velocity, $(\delta V_l/V_{l,0})_{\mathrm{anh}}$, for $(\mathrm{Li_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (Δ) and $(\mathrm{K_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (▲) glasses.

Since static inhomogeneities affect negligibly the velocity (Brillouin shift) measurements, to describe the temperature behavior of the hypersound velocity V_l over the whole temperature range between 20 and 300 K, it is sufficient to write an expression which cover both relaxation and anharmonic contributions only:

$$(\delta V_l/V_{l,0}) = (\delta V_l/V_{l,0})_{\mathrm{rel}} + (\delta V_l/V_{l,0})_{\mathrm{anh}}, \tag{6}$$

where $(\delta V_l/V_{l,0})_{\mathrm{rel}}$ is given by Eq. (5). The temperature behaviors of $(\delta V_l/V_{l,0})_{\mathrm{rel}}$ have been determined using the parameters obtained by the numerical evaluation of the relaxation loss in Eq. (5); they are shown as dotted (LiBO) and dashed (KBO) lines in Fig. 2(b). Subtraction of the latter contribution from the experimental data of sound velocity leads to temperature dependences of $(\delta V_l/V_{l,0})_{\mathrm{anh}}$ reported in Fig. 4(b).

Analysis of the anharmonic contributions, Q^{-1}_{anh} and $(\delta V_l/V_{l,0})_{\mathrm{anh}}$, has been performed by following the procedure described in Ref. 2, where some results of the theory concerning the interaction of sound waves with thermal phonons in dielectric crystals[14,24–26] have been extended to glassy solids:

$$Q^{-1}_{\mathrm{anh}} = A\frac{\omega\tau_{\mathrm{th}}}{1+\omega^2\tau_{\mathrm{th}}^2}, \tag{7}$$

$$\left(\frac{\delta V_l}{V_{l,0}}\right)_{\mathrm{anh}} = -\frac{A}{2}\frac{1}{1+\omega^2\tau_{\mathrm{th}}^2}, \tag{8}$$

where

$$A(T) = \frac{\gamma_G^2 C_V T V_l}{2\rho V_D^3}, \tag{9}$$

where γ_G is the mean acoustic-mode Grüneisen parameter, C_V is the specific heat per unit volume, V_D is the Debye velocity, and τ_{th} is the mean lifetime of the thermal vibrations. It is worth noting that in crystals, the validity of both Eqs. (7) and (8) is limited to the high-temperature region, where Λ and the mean free path of thermal modes is shorter than the acoustic wavelength, that is, the region of the *Akhiezer loss or phonon viscosity*.[27] At low temperatures, where $\omega\tau_{\mathrm{th}} \gg 1$, quantum effects become dominant and the theory of Landau and Rumer,[28] which describes the interactions between sound waves and thermal modes in terms of phonon-phonon collisions, is more appropriate.

When $\omega\tau_{\mathrm{th}} \ll 1$, Eqs. (7) and (8) become

$$Q^{-1}_{\mathrm{anh}} = A\omega\tau_{\mathrm{th}}, \tag{10}$$

$$\left(\frac{\delta V_l}{V_{l,0}}\right)_{\mathrm{anh}} = -\frac{A}{2}. \tag{11}$$

At hypersonic frequencies, i.e., the range explored by Brillouin scattering spectroscopy, the condition $\omega\tau_{\mathrm{th}} \ll 1$ is surely satisfied for $T > 100$ K. Measurements of thermal conductivity Λ on LiBO glass,[29] in fact, give a value of τ_{th} of 1.8×10^{-11} s at 10 K, a temperature which lies within the plateau region of Λ, where the dominant phonon approximation should be valid.[5,30]

Equation (11) permits a direct assessment of the temperature behaviors of $A(T)$ [see Fig. 5(a)], which show a smooth linear increase with increasing temperature for both the glasses. In order to estimate the mean acoustic-mode Grüneisen parameter γ_G by the relation defining $A(T)$, the specific heats per unit volume C_V have been combined with the Debye velocities V_D,[8] the longitudinal hypersonic velocities V_l, and the densities ρ, with all these quantities measured at the same temperatures of the values of $A(T)$ reported in Fig. 5(a). The obtained values of $\gamma_G(T)$ are shown in Fig. 5(b); they exhibit a temperature-independent behavior in KBO and a slight increase with decreasing temperature in LiBO. An important result of the present analysis is that the room-temperature values of γ_G (0.89 in KBO and 1.13 in LiBO) are in very close agreement with the value of 0.91 of the longitudinal-acoustic-mode Grüneisen parameter $\gamma_{G,l}$ determined by ultrasonic measurements (megahertz range) under pressure on $(\mathrm{Ag_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ glass.[31] As clearly proved by NMR measurements,[32] the borate network of the latter glass has the same short-range structure of the alkaline borate glasses investigated in this study. Therefore, similar characteristics of vibrational anharmonicity in close frequency intervals should be expected.

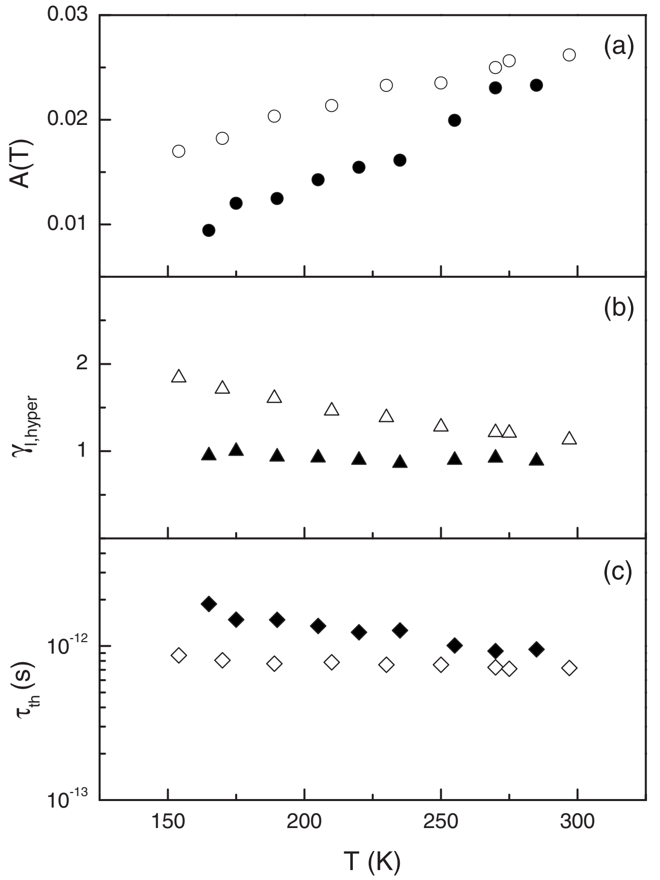

FIG. 5. (a) Temperature dependence of the strength of the anharmonic contribution, $A(T)$, for $(\mathrm{Li_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (○) and $(\mathrm{K_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (●) glasses. (b) Temperature dependence of the mean Grüneisen parameter γ_G determined at hypersonic frequencies for $(\mathrm{Li_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (Δ) and $(\mathrm{K_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (▲) glasses. (c) Temperature dependence of the mean lifetime of the thermal vibrations, τ_{th}, determined at hypersonic frequencies for $(\mathrm{Li_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (◇) and $(\mathrm{K_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$ (◆) glasses.

This finding represents a really important result of the present analysis because it proves that the anharmonic interactions between hypersonic waves and thermal modes contribute substantially to the behaviors of the sound velocity and, consequently, of the internal friction in the temperature region where the Akhiezer mechanism of thermal vibration viscosity is dominant.

Finally, using the values of $A(T)$ and Q^{-1}_{anh} in Eq. (10), we have calculated the values of τ_{th} which are reported in Fig. 5(c). For both the borate glasses, τ_{th} decreases with increasing temperature, exhibiting a room-temperature value with a magnitude on the order of 10^{-13} s. We would like to remark, however, that the above evaluation of τ_{th} must be regarded as highly tentative mainly for the following reasons:

(i) Q^{-1}_{anh} has been determined by a procedure implying the subtraction of an attenuation background due to static inhomogeneities which represents a substantial fraction of the experimental internal friction; and

(ii) the high-temperature dynamics of thermal modes in a glass is a too complex argument to be described adequately by a single parameter.

V. CONCLUSIONS

We have studied the acoustic behaviors of two borate glasses with the same concentration of alkali oxide but different cations (lithium and potassium) by Brillouin scattering experiments over the temperature range between 15 and 300 K. The analysis of the hypersonic loss curves show that different static and dynamic mechanisms contribute to the sound attenuation: (i) a temperature-independent attenuation background due to the presence of density fluctuations within the scattering volume, (ii) the localized motion of defect states, and (iii) the vibrational anharmonicity. Assuming that the structural defects transform their local motion from tunneling to thermally activated jumps with increasing temperature, it has been possible to evaluate the attenuation background. The temperature dependences of the hypersonic loss are characterized by a peak, whose temperature T_{peak} well fits the Arrhenius plot determined by the ultrasonic peak temperatures. This has been considered as a clear indication that thermally activated relaxations of the defect states, which mainly determine the ultrasonic loss in the same glasses above 20 K, also contribute to the hypersonic loss. The evaluation of the relaxation contributions to the hypersonic loss and sound velocity by the ADWP model permits the assessment of the temperature behaviors of the internal friction and sound velocity due to the anharmonic interactions between the hypersonic waves and thermal vibrations. This leads to the quantitative evaluation of mean acoustic-mode Grüneisen parameter γ_G in the temperature region where the acoustic behaviors should be governed by the Akhiezer mechanism of thermal vibration viscosity. The obtained value is in very close agreement with the elastic Grüneisen parameter determined by ultrasonic measurements under pressure in a glass characterized by the same borate network. This finding proves that, besides classical activation of structural defects, vibrational anharmonicity plays a significant role in governing the acoustic behaviors in the gigahertz range.

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