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Microscopic origin of low-energy excitations in superionic glasses

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A low-temperature ultrasonic study of AgI-Ag_2O-B_2O_3 superionic glasses is presented. We show that for $T < 10$ K the acoustic behavior is governed by the two-level-system (TLS) phonon-assisted relaxation. The analysis of the sound-velocity data seems to suggest that TLS-phonon interactions are essentially governed by a two-phonon or first-order Raman relaxation process for $T > 3$ K. The TLS density of states $\bar{P}$ does not follow the recently proposed empirical law, that $\bar{P}$ should be an exponentially increasing function of T_G^{-1}, T_G being the glass transition temperature. By calculating the tunneling frequency for the silver ions, which are subjected to thermally activated jumps at high temperatures ($T > 77$ K), values have been obtained which exclude them as a microscopic origin of TLS's, and some alternative hypotheses are proposed.

I. INTRODUCTION

The AgI-Ag_2O-B_2O_3 glassy systems are a class of fast-ionic conductors, characterized by high mobility of silver ions.[1] A preliminary investigation of the low-temperature acoustic attenuation in some of the cited glasses[2] emphasized the existence of the typical anomalies of the glassy solids,[3] which are generally attributed to localized low-energy excitations. These excitations are well explained in terms of the tunneling model[4,5] which presumes the presence in the network of single atoms or groups of atoms, having two different equilibrium positions (double-well potential description). At low-temperature, transitions between the positions are made possible by tunneling, and the interactions with phonons give rise to resonant and relaxational effects.[6]

In superionic glasses the silver ions are subjected, at high temperatures ($T > 77$ K), to thermally activated jumps between available sites in the network, as revealed from the acoustic losses and dispersions, due to ionic migration effects.[7,8]

This peculiarity suggested the possibility of explaining all of the acoustic behavior in superionic glasses, involving silver ions: tunneling motions at low temperatures and thermally activated jumps at high temperatures. Such an attribution seemed very attractive, because it would have supplied an unitary explanation on the microscopic origin of the observed acoustic anomalies in these glasses.

Now the tunneling frequency $\Omega/2\pi$ can be calculated by the following relation:[9]

$$\Omega=\omega_0 e^{-\lambda}, \quad \lambda=d(2mV)^{1/2}\hbar^{-1} \tag{1}$$

d being the distance between two Ag sites, m the mass of a tunneling silver atom, V the height of the potential-energy barrier between the two minima corresponding to two Ag sites, and ω_0 is of the order of the oscillator frequency. Inserting the values of V and d, obtained by a recent detailed analysis of the migration losses in AgI-Ag_2O-B_2O_3 glasses,[7] for all the glasses we obtain a magnitude order of λ of about 10^2, corresponding to $e^{-\lambda}\approx 0$. Taking the existence of a barrier-height distribution[7] also into account, such values undoubtedly seem to exclude the possibility of tunneling for the silver ions, which are responsible for the fast conduction processes at high temperatures.

Similar conclusions were inferred from an ultrasonic study on a class of lithium-based superionic glasses:[10] it was proved that the two-level-system (TLS) density is independent from the lithium ion density. In order to have a better understanding of the question regarding the TLS microscopic origin in superionic glasses, we present here the results of a low-temperature ultrasonic study on the $(AgI)_x[(Ag_2O)_y(B_2O_3)_{1-y}]_{1-x}$ glasses and we will discuss them in the light of the current theories of TLS.

II. PREPARATION OF SAMPLES AND EXPERIMENTAL DETAILS

Different compounds of the $(AgI)_x[(Ag_2O)_y(B_2O_3)_{1-y}]_{1-x}$ glassy system, x and y being the molar fractions, were analyzed. The details, concerning the preparation and the appropriate storage to prevent any possible contamination, have been underlined elsewhere.[1,7]

Ultrasonic measurements in the 15–85-MHz frequency range, both for longitudinal and shear waves, were performed in the 1.5–35-K temperature range by the same experimental setup and procedure previously described.[2,7] All the attenuation data presented have been corrected for an average diffraction loss λ/a^2 dB cm^{-1}, λ being the ultrasonic wavelength and a the transducer radius. The contribution to the loss of the bonding agent between the transducer and the sample was neglected, because its typical thickness was lower than 4 μm.

III. RESULTS AND DISCUSSION

A. Acoustic attenuation

The temperature behavior of the acoustic attenuation in the glass with $x = 0.0$ is shown in Fig. 1(a) (longitudinal waves) and Fig. 1(b) (shear waves). Similar behaviors are also observed in other glasses studied. It is evident that the acoustic attenuation initially increases quite sharply with the temperature with a frequency-dependent slope and in the intermediate-temperature region it presents a plateau; which is also frequency dependent. The presence of a plateau in the acoustic attenuation was theoretically predicted by Jackle[6] in the frame of the "TLS-phonon-assisted relaxation." In this process the acoustic wave interacts with TLS's, modifying their thermal equilibrium population and a new equilibrium distribution will be reached by the cooperation of thermal phonons in a characteristic relaxation time T_1, that in the case of a one-phonon or direct process is given by[6,11]

$$T^{-1}=rK_3T^3(E/2kT)^3\coth(E/2kT)\ , \tag{2}$$

where

$$K_3=\frac{4k_B^3}{\pi\rho\hbar^4}\sum_i \gamma_i^2/V_i^5\ ,$$

with index i referring to the different polarizations (one longitudinal and two transverse). In Eq. (2) the TLS splitting energy E is equal to $(\Delta_0^2+\Delta^2)^{1/2}$, Δ_0 being the tunneling energy and Δ the eventual asymmetry of the double-well potential; γ_i are the deformation potentials, v_1 and v_t are the longitudinal and transverse sound wave velocities, and ρ is the density. The parameter $r=(\Delta_0/E)^2$ ranges between a minimum value $r_{\rm min}$ and 1 (giving rise, as a consequence, to a T_1 distribution) to take the existence of a coupling constants distribution into account, arising from the randomness of the network. An attenuation of the sound waves results from this process, which can be expressed as[11]

$$\alpha_i=\frac{\bar P\gamma_i^2}{\rho v_i^3}\int_0^\infty d(E/2kT)\,\text{sech}^2(E/2kT)\times\int_{r_{\rm min}}^1 dr(1-r)^{1/2}r^{-1}\frac{\omega^2T_1}{1+\omega^2T_1^2}\ , \tag{3}$$

where $\bar P$ is the constant density of states of the TLS and ω the angular sound frequency. It has been usual practice to assume without concrete justification that the standard tunneling distribution works for all glasses.[3,10-12] In the limit of high temperatures when $\omega T_1^{\rm min}\ll 1$ [$T_1^{\rm min}$ is the minimum value of T_1 and it corresponds to set $r=1$ in the Eq. (2)], Eq. (3) gives[6]

$$\alpha_i=\pi\left[\frac{\bar P\gamma_i^2}{2\rho v_1^3}\right]\omega=\frac{\pi}{2v_i}C_i\omega \tag{4}$$

and at low temperatures, when $\omega T_1^m \gg 1$, Eq. (3) leads to

$$\alpha_i=\frac{\pi^4}{96}\left[\frac{\bar P\gamma_i^2}{\rho v_i^3}\right]K_3T^3\ . \tag{5}$$

In our glasses the T-independent acoustic absorption, proposed by Eq. (4), is clearly evident but the linear frequency dependence does not seem to have been exactly verified, see Fig. 2. This circumstance arises, of course, from the presence of a temperature-independent but frequency-dependent background, which must be sub-

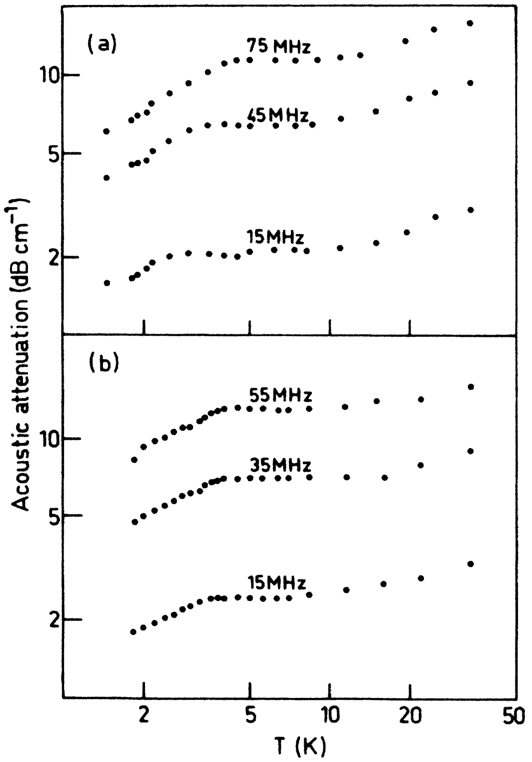

FIG. 1. Typical temperature behavior of acoustic attenuation in $(\text{AgI})_x[(\text{Ag}_2\text{O})_y(\text{B}_2\text{O}_3)_{1-y}]_{1-x}$: (a) longitudinal waves; (b) shear waves.

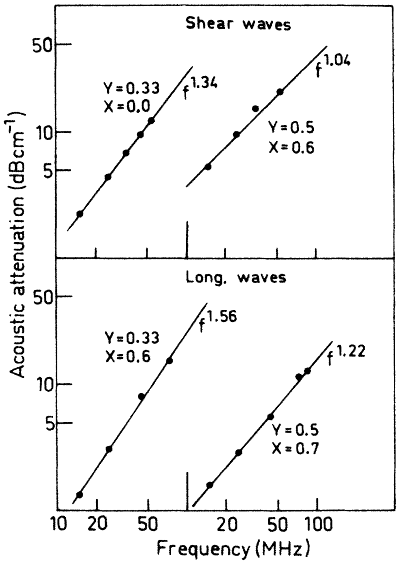

FIG. 2. Typical logarithmic plot of the acoustic attenuation vs frequency in the temperature region of the plateau for $(\text{AgI})_x[(\text{Ag}_2\text{O})_y(\text{B}_2\text{O}_3)_{1-y}]_{1-x}$ glasses. Note the shift of the horizontal scale beginning for the different samples.

tracted from the experimental data in order to quantitatively evaluate the contribution of the TLS relaxation process. We can in advance discard the influence of the ultrasound–thermal-phonon interaction, because its contribution is insignificant at this temperature and frequency range.[13]

Other insignificant acoustic losses which are added to those of microscopic origin could arise from some degree of the sample faces nonparallelism (eventually induced by the presence of a bonding agent) and also from the scattering of ultrasounds, due to small inhomogeneities, as pores (voids) or precipitates (in multicomponent glasses). However, both these loss sources have been evaluated[14] and it results in an attenuation proportional to f^2 for the former and to f^4 for the latter, in the case of the Rayleigh approximation.

Considering that the wavelength of ultrasounds used varies in the range between 30 and 300 μm and that the studied glasses (which are sufficiently transparent) appear to be very homogeneous, the Rayleigh condition is shown to be completely satisfied. Thus only the TLS relaxation gives a linear contribution to the frequency dependence of the acoustic attenuation in the temperature region of the plateau. In Fig. 3 we report a typical plot of α/f as a function of f in the plateau region, both for longitudinal and shear waves. A linear behavior of α/f is evident which corresponds to an f^2 contribution as dominant in the background attenuation. Of course the extrapolation of the curve at $f=0$ furnishes the coefficient of the linear term in the frequency dependence of the acoustic attenuation, whose expression is given by Eq. (4).

The values of C_i for the various glasses are inserted in Table I. By the expression of C_i, it was possible to calculate the product $\bar{P}\gamma_i^2$, also inserted in Table I with the values of ρ and v.

By subtracting the acoustic background from the experimental data, it is possible to verify the $\omega^0 T^3$ behavior [see Eq. (5)] with the decreasing temperature. The corresponding plot is shown in Fig. 4 for one of the glasses studied, as typical: a deviation of the low-temperature data from the $\omega^0 T^3$ curve is evident, indicating the location of the $\omega T_1^m \gg 1$ region at lower temperatures.

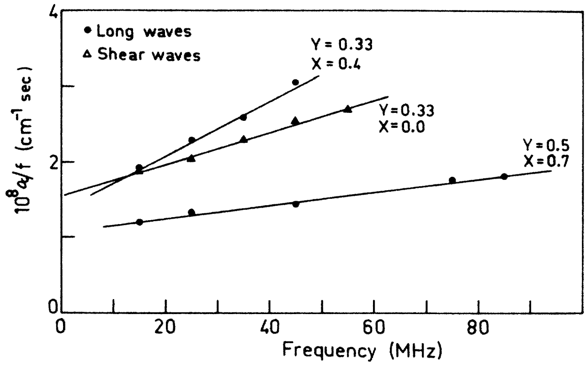

FIG. 3. Typical frequency behavior for the $(\mathrm{AgI})_x[(\mathrm{Ag_2O})_y(\mathrm{B_2O_3})_{1-y}]_{1-x}$ of the ratio between the acoustic attenuation and the ultrasound frequency in the temperature region of the plateau.

In Fig. 4 we also show, as a continuous line, the result of the experimental data best fit by Eq. (3) and by using $\bar{P}\gamma_i^2$ and K_3 as free parameters in a MINUIT minimum search program.

The obtained values of $\bar{P}\gamma_i^2$ and K_3 are 2.2×10^9 ergs cm^{-3} and 1.12×10^9 K^{-3}s^{-1}, respectively. The value of $\bar{P}\gamma_i^2$ is practically the same one deduced by the application of Eq. (4) in the plateau temperature region (see Table I). However, the agreement between the theoretical curve and the experimental data is quite good in the plateau region, but not satisfactory where the acoustic attenuation shows a bending. Probably TLS-phonon interactions, more complicated than the direct ones, must be taken into account.[11] This peculiarity will be confirmed by the sound-velocity behavior analysis discussed later. We have similar situations for the other frequencies investigated and in other glasses.

TABLE I. Values of density ρ, sound velocities V, parameters C and $\bar{P}\gamma_i^2$ [see Eq. (3)], coupling constant γ_1, TLS density of states $\bar{P}$, and glass transition temperature T_G for $(\mathrm{AgI})_x[(\mathrm{Ag_2O})_y(\mathrm{B_2O_3})_{1-y}]_{1-x}$ glasses. The values of sound velocities refer to longitudinal waves when not pointed out and always at 1.8 K. The values of ρ and T_G are those of Ref. 1.

x	ρ (g cm^{-3})	V (m s^{-1})	C ($\times10^4$)	$\bar{P}\gamma_i^2$ (10^8 ergs cm^{-3})	γ_1 (eV)	$\bar{P}$ (10^{32} ergs^{-1} cm^{-3})	T_G (K)
				$y=0.33$			
0.0	4.03				0.72	3.36	663
	long	4420	5.68	4.47			
	shear	2298	3.78	0.81			
0.4	4.66	3773	5.15	3.42	0.69	2.79	630
0.6	4.84	3301	2.63	1.39	0.65	1.28	606
				$y=0.5$			
0.3	5.42	3850[a]	7.63	6.13	0.63	6.02	588
0.6	5.76				0.56	2.58	523
	long	2952	4.13	2.07			
	shear	1404	6.27	0.72			
0.7	5.82	2670	3.01	1.25	0.55	1.61	513

[a] Extrapolated value (see Ref. 7)

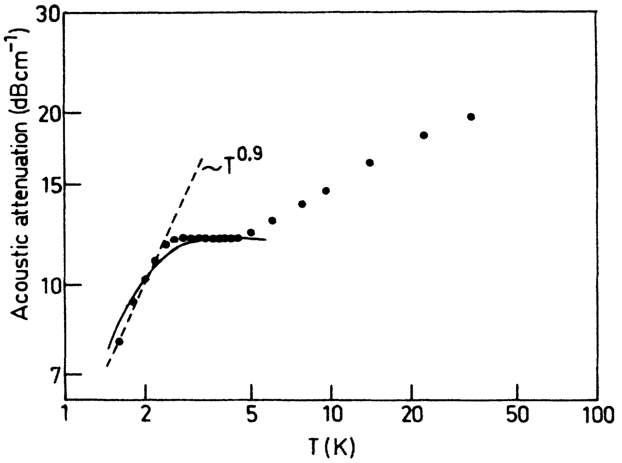

FIG. 4. Logarithmic plot of the acoustic attenuation arising from the TLS relaxation in the glass with $y=0.5, x=0.6$. The continuous line corresponds to the theoretical fit by Eq. (3) (see text). The dashed line has a slope of about 0.9.

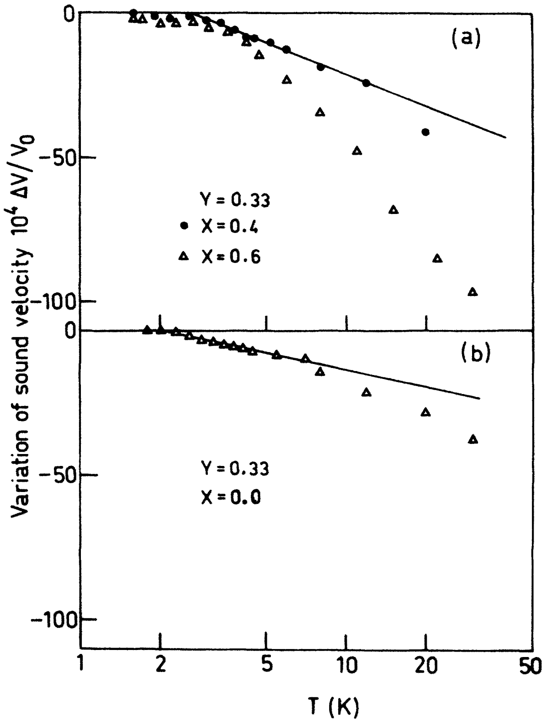

FIG. 5. Fractional sound velocity of 15-MHz longitudinal waves as a function of temperature in $(\mathrm{AgI})_x[(\mathrm{Ag_2O})_{0.33}(\mathrm{B_2O_3})_{0.67}]_{1-x}$ glasses: (a) longitudinal waves; (b) transverse waves. The continuous lines have a slope of -15.6×10^{-4} in (a) and of -9.5×10^{-4} in (b).

B. Sound velocity

In Fig. 5 the temperature dependence of the sound-velocity fractional variation $\Delta v/v=[v(T)-v_0]/v_0$ is shown, v_0 being the value at the lowest temperature for various glasses.

The following peculiarities are revealed.

1. In the region of the lowest temperatures ($T<3$ K) the sound velocity is about almost constant in all the glasses.
2. For $T>3$ K in the glasses with $x=0.0$ and $x=0.4$, the velocity first shows a logarithmic decrease with the temperature and then it tends to bend; in the glass with $x=0.6$ it always has a decreasing behavior with the temperature, but with a continuously changing slope.

Three physical mechanisms could contribute to the velocity behavior in this temperature range: the TLS resonance, the TLS relaxation, and the anharmonicity.

The anharmonic contribution[15,16] will be very small for $T<30$ K, taking also into account the similarity (as order of magnitude) of the average Grüneisen parameters in crystals and in glasses.[17,18,19] As a consequence it can be neglected.

The temperature dependence of $\Delta v/v$, due to the overlap of other two contributions, when $\omega T_1^m \ll 1$, can be written as[3,11]

$$\Delta v/v=-nC_i\ln(T/T_0)\ , \tag{6}$$

T_0 being an arbitrary reference temperature. The parameter n will be equal to $\frac{1}{2}$ in the case of a direct or one-phonon process and to $\frac{5}{2}$ in the case of a first-order Raman or two-phonon process.[11]

Now the condition $\omega T_1^m \ll 1$ is satisfied in all the samples for $T>3$ K, when $f=\omega/2\pi=15$ MHz, as can be checked from the attenuation data. In fact, above 3 K we find a logarithmic decrease with the temperature of $\Delta v/v$ in the glasses with $x=0.0$ and $x=0.4$, whose slope (continuous line in Fig. 5) is, respectively, -9.5×10^{-4} and -15.6×10^{-4}. Both these values are very near $\frac{5}{2}$ of the corresponding C_i, see Table I, and this circumstance seems to indicate that at "high temperatures" ($\omega T_1^m \ll 1$) the dominant process in the TLS-phonon-assisted relaxation is a two-phonon process.

In the glass with $x=0.6$ the lack of a temperature logarithmic decrease of $\Delta v/v$ is probably due to the onset of a thermally activated relaxation characterized by low activation energies, whose low-temperature tail should mask the contribution of the TLS relaxation. Evidence for this relaxation, whose temperature location at ultrasonic frequencies is between 4.2 and 77 K, appears from the low-temperature acoustic behavior in glasses of the same series[19] and in sodium borate glasses.[20] Moreover, the shape of the $\Delta v/v(T)$ curve in the glass with $x=0.6$ above 6 K seems typical of a dispersive behavior. In the glasses with a lower AgI content the location of this relaxation should be shifted at higher temperatures, avoiding its observation in the explored temperature range and also its overlapping on the TLS relaxation. More research is at present in progress to verify these last suppositions.

C. TLS density of states and glass transition temperature

It has been established that there is an empirical connection between the glass transition temperature T_G and the TLS density of states $\bar{P}$.[22] To find out if this connection also exists in these superionic glasses, it is necessary to know $\bar{P}$ which can be obtained from the measured products $\bar{P}\gamma_i^2$ given in Table I. Hence an assessment of the corresponding values of the coupling constants γ_i is needed. In principle it is possible to obtain γ_i and $\bar{P}$ from complete measurements of ultrasonic attenuation and velocity at very low temperature but we do not have access to that technology.

However, there is an alternate procedure which can be used to assess the γ_i values from the recently proposed empirical law which provides a roughly linear correlation between the coupling constants and the glass transition temperature T_G for a wide range of amorphous materials.[21,22]

As already described by Reichert *et al.*,[22] we have plotted the known values of γ_i for various glasses as a function of each corresponding T_G in Fig. 6; despite a lot of scatter in the data, a clear trend of increase of the coupling constants with increased T_G can be seen.

By using the T_G values of our glasses,[1] we have been able to extract the corresponding coupling constants γ_i (given in Table I) from the best linear fit to the data shown as a continuous line in Fig. 6. It is worth observing that γ_i obtained are very near to those directly determined from experiment in another type of ionic conductors: the lithium-based borate glasses.[10] The TLS densities of states $\bar{P}$, consequently obtained are also inserted in Table I.

Now it clearly results that $\bar{P}\gamma_1^2$ and also the TLS spectral density $\bar{P}$ decrease with the AgI content, and consequently with T_G (see Table I) for the glasses with $y=0.5$ and $y=0.33$.

Recently Reichert *et al.*[22] have proposed that $\bar{P}$ and T_G are related by the following relation:

$$\bar{P}=\bar{P}_0\exp(\Delta/kT_G)\ , \tag{7}$$

where $\bar{P}_0=5.5\times10^{31}$ ergs^{-1} cm^{-3} and $\Delta/K=630$ K.

The ionic glasses studied do not follow these empirical law (an exponential increase of $\bar{P}$ with T_G^{-1}). Moreover, the relation does not give the magnitude of the values of $\bar{P}$, even taking into account the assumption used to get them: for example for the glass without AgI ($T_G=663$ K), by Eq. (7) we obtain a value for $\bar{P}$ of 1.42×10^{32} ergs^{-1} cm^{-3}. Similar remarks also arise from the analysis of the $\bar{P}$ values in lithium-borate glasses (see Table II in Ref. 10): $\bar{P}$ increases with T_G (the only exception being the glass with 0.25 Li_2O) and its value is quite higher than the one excepted by Eq. (7).

Now the anomalous behavior of $\bar{P}$ with T_G, shown by AgI-Ag_2O-B_2O_3 glasses, could be explained by the actual structural hypothesis on these systems.

As a matter of fact it has been inferred[7,23] that the silver iodide slightly affects the random network of borate glass (Ag_2O-B_2O_3) and it gives rise to the formation of microdomains, weakly bonded to the host matrix, that remind one of crystalline AgI on a local scale. From this point of view the relevant contribution to the TLS spectral density would be the one of the Ag_2O-B_2O_3 matrix and as a consequence $\bar{P}$ will decrease with the AgI content. Following such an interpretation, we can try to identify the TLS as arising from some kind of local motion involving particular atomic units, present in the borate matrix. Tentatively we can suggest that these motions could be connected to some microscopic rearrangements of the tetrahedical BO_4 groups and of nonbridging oxygens, which are formed in increasing numbers, when Ag_2O (or generally an alkaline metallic oxide) (Ref. 24) is added to the boron dioxide. However these suggestions need a more clear support, as we should be able to obtain, by extending our research to other glasses of the $(Ag_2O)_y(B_2O_3)_{1-y}$ system.

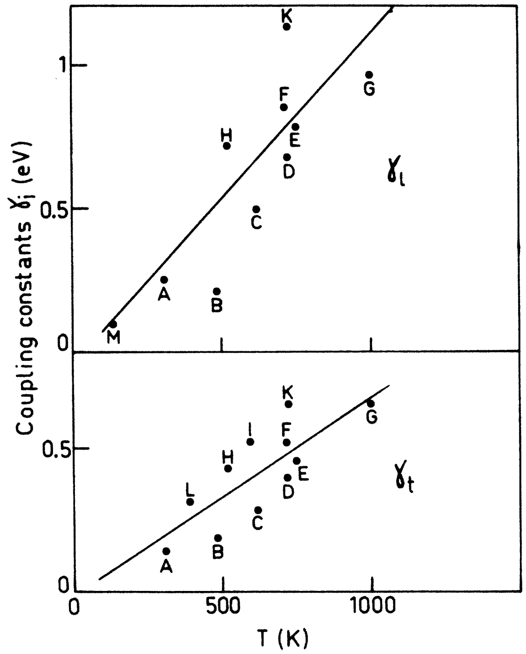

FIG. 6. Behavior of the deformation potentials γ_i vs the glass transition temperature, as coming out from the actual experimental knowledge. A: selenium (Ref. 22); B: B_2O_3 (Ref. 10); C, D, E, and F: lithium-borate glasses (Ref. 10); G: BK7 (Ref. 21); H, I, and K: fluorozirconate glasses BALNA, V52, and LAT (Ref. 21); PMMA (Ref. 22); amorphous water (Ref. 22). The continuous lines come out from the best linear fit.

IV. CONCLUSIONS

A low-temperature ultrasonic study of AgI-Ag_2O-B_2O_3 glasses reveals the presence of anomalies in the acoustic attenuation and in the sound velocity, which are well explained in terms of the TLS-phonon assisted relaxation.

The sound-velocity behaviors seem to indicate, as dominant in the $\omega T_1^m \ll 1$ temperature region, a two-phonon or first-order Raman relaxation process. The values of the TLS density of states $\bar{P}$ and their behavior as a function of the AgI content and, as a consequence of T_G, do not follow an empirical law which proposes an exponential connection between $\bar{P}$ and T_G^{-1}. It is argued that in ionic glasses T_G is not the only parameter which determines the TLS density of states and it is probably necessary to introduce some other parameter which takes the stoichiometry of the glass into account.

Finally it has been deduced that the mobile silver ions, which cause migration losses at higher temperatures, cannot be considered as a microscopic origin of TLS. In this connection the behavior of $\bar{P}$ as a function of the AgI content seems to suggest that only the borate matrix contributes to the formation of two-level systems.

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[1] G. Chiodelli, A. Magistris, M. Villa, and J. Bjorkstam, J. Non-Cryst. Solids **51**, 143 (1982).

[2] G. Carini, M. Cutroni, M. Federico, G. Galli, G. Tripodo, and A. Avogadro, Physica B + C **107B**, 175 (1981).

[3] S. Hunklinger and M. V. Schickfus, in *Amorphous Solids—Low Temperature Properties*, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981), p. 81; S. Hunklinger and A. K. Raychaudhury, in *Progress in Low Temperature Physics*, edited by D. F. Breuer (North-Holland, Amsterdam, 1986), Vol. IX, p.265.

[4] P. W. Anderson, B. L. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

[5] W. A. Phillips, J. Low. Temp. Phys. **7**, 351 (1972).

[6] J. Jackle, Z. Phys. **257**, 212 (1972).

[7] G. Carini, M. Cutroni, M. Federico, and G. Tripodo, Phys. Rev. B **32**, 8264 (1985); **30**, 7219 (1984), and references therein.

[8] C. Liu, H. G. K. Sundar, and C. A. Angell, Solid State Ionics **18-19**, 442 (1986).

[9] W. A. Phillips, in *Amorphous Solids—Low Temperature Properties*, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981), p. 1.

[10] M. Deveaud, J. Y. Prieur, and W. D. Wallace, Solid State Ionics **9-10**, 593 (1983).

[11] P. Doussineau, Ch. Frenois, R. Leisure, A. Levelut, and J. Y. Prieur, J. Phys. (Paris) **41**, 1193 (1980).

[12] D. Ng and R. J. Sladek, Phys. Rev. B **11**, 4017 (1975).

[13] H. J. Maris, in *Physical Acoustics*, edited by P. Mason and R. Thurston (Academic, New York, 1971), Vol. 8, p. 279.

[14] R. Truell, C. Elbaum, and B. B. Chick, *Ultrasonic Methods in Solid State Physics* (Academic, New York, 1969), p. 107.

[15] J. A. Garber and A. V. Granato, Phys. Rev. B **11**, 3990 (1975).

[16] G. A. Alers, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1966), Vol. IV A, p. 277.

[17] W. A. Phillips, in *Amorphous Solids*, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981), p. 53.

[18] G. K. White, Cryogenics **4**, 2 (1964).

[19] G. A. Saunders, H. A. A. Sidek, J. D. Comins, G. Carini, and M. Federico, Philos. Mag. B **56**, 1 (1987).

[20] J. T. Krause and C. R. Kurkjan, in *Borate Glasses*, edited by L. D. Pye, V. D. Frechette, and N. J. Kreidl (Plenum, New York, 1978), Vol. 12, p. 577.

[21] P. Dossineau, M. Matecki, and W. Schon, J. Phys. (Paris) Colloq. **43**, C9-493 (1982).

[22] N. Reichert, M. Schmidt, and S. Hunklinger, Solid State Commun. **57**, 315 (1986), and references therein.

[23] G. Carini, M. Cutroni, A. Fontana, G. Mariotto, and F. Rocca, Phys. Rev. B **29**, 3567 (1984).

[24] P. J. Bray and J. G. O'Keefe, Phy. Chem. Glasses **4**, 37 (1963); K. S. Kim and P. J. Bray, J. Nonmetals **2**, 95 (1974).