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^{11}B spin-lattice relaxation and disorder modes in ionic glassy conductors $(AgI)_x(Ag_2O \cdot nB_2O_3)_{1-x}$

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The temperature and frequency dependence of the ^{11}B nuclear spin-lattice-relaxation rate has been investigated in a number of ionic glassy conductors of general composition $(AgI)_x(Ag_2O \cdot nB_2O_3)_{1-x}$, with $n=1$, 2 and variable x. At $T>100$ K a BPP-type maximum in T_1^{-1} is found that is consistent with a thermally activated reorientational motion of BO_4 groups. [BPP indicates Bloembergen, Percell, and Pound, Phys. Rev. 73, 679 (1948).] It is found that the sum of the activation energy for BO_4 motion with the activation energy recently measured for Ag^+ local motion is equal to the activation energy derived from conductivity measurements. At low temperature one observes the usual quasilinear temperature dependence of T_1^{-1} and an unusual frequency dependence not described by a power law. An interpretative model of nuclear relaxation due to disorder modes is developed to explain the frequency dependence. The analysis of the data indicates the presence of a relatively large number of slowly fluctuating two-level systems, formed by coupled BO_4 units, responsible for the frequency dependence of the experimental relaxation rate.

I. INTRODUCTION

Ionic conductors containing AgI can be prepared in the form of glasses and they exhibit ionic conductivity as high as 10^{-1}–10^{-2} (Ω cm) at room temperature.[1,2] The microscopic mechanisms leading to this high conductivity are still not completely understood. Furthermore, the occurrence of high ionic conduction in glassy matrix poses the interesting possibility of a coupling[3] between the translational degrees of freedom of the Ag ions and the disorder modes or two-level systems (TLS's) typical of glassy materials.[4,5] In this paper we use the ^{11}B nuclear spin-lattice-relaxation rate, T_1^{-1} as a probe of the microscopic dynamics of the glass-forming borate units. The temperature dependence of T_1^{-1} at "high temperature," i.e., $T>100$ K, yields information about the local atom motion of the borate units and the corresponding activation energy. At low temperature, the relaxation rate is dominated by the fluctuations of electric-field gradient (EFG) associated with the tunneling motion of the atoms or groups of atoms forming the TLS's. The microscopic origin of the TLS's and the exact process by which the nuclear spins are relaxed by TLS's are still unsettled problems. We find that the nuclear spin-lattice-relaxation model developed by Szeftel and Alloul,[6] when properly extended to include the effect of slow fluctuating TLS's, yields the best framework to analyze the data. We obtain expressions for the temperature and frequency dependence of T_1^{-1} that are in good agreement with the experimental data and allow one to derive information about the size, the number, and the fluctuating time of the TLS's.

II. EXPERIMENTAL DETAILS

The compounds were prepared from certified reagent-grade AgI, $AgNO_3$, and B_2O_3 as described elsewhere.[1] The samples investigated here are of the general composition $(AgI)_x(Ag_2O \cdot nB_2O_3)_{1-x}$. The results on ^{11}B NMR refer mostly to compounds with $n=2$ ($x=0.0$, 0.2, 0.5, 0.65), which have been investigated by means of specific-heat measurements.[7] A few results of ^{11}B relaxation rate refer to samples with $n=1$ ($x=0.2$, 0.8), which have already been in part published.[3] The measurements were performed by using a Fourier transform (FT) pulse spectrometer operating at variable frequency (3–80 MHz) in connection with both a 6-T superconducting magnet and a standard electromagnet. The ^{11}B NMR line is broadened by second-order quadrupole effects, as can be seen by the inverse frequency dependence of the width. At a resonance frequency $\nu_L=10$ MHz one finds a width at half intensity $\Delta\nu \cong 5$ kHz in reasonable agreement with a quadrupole coupling frequency of $\nu_Q \cong 0.2$ MHz, as measured for ^{11}B in the BO_4 group that is the most important boron group in our samples.[8] Since the NMR line is inhomogeneously broadened, the T_1 measurements were performed on the echo signal following a $(\pi/2)_x$-$(\pi/2)_y$ pulse sequence. The recovery of the nuclear magnetization was monitored after a short ($t \ll T_1$) saturating pulse sequence that is believed to saturate the central line transition ($-\frac{1}{2} \leftrightarrow +\frac{1}{2}$) without affecting the remaining levels. Under these initial conditions one has, from the solutions of the master equations[9]

$$\frac{M(t)-M(\infty)}{M(\infty)}=\tfrac{1}{2}\exp(-2W_1t)+\tfrac{1}{2}\exp(-2W_2t) , \quad (1)$$

where W_1 and W_2 are the probabilities for the transition with $\Delta m=1$ and 2, respectively. A few measurements were also performed with a long saturating pulse sequence ($t \gg T_1$) for which one expects[10]

$$\frac{M(t)-M(\infty)}{M(\infty)}=\exp(-2W_2t) . \quad (2)$$

The recovery law in both cases is practically the same, indicating that $W_1 \cong W_2 \cong W_Q$. Thus we assume that the measured relaxation rate $T_1^{-1} = 2W_Q$. In some instances we found a slight nonexponential decay that should be ascribed to a macroscopic distribution of relaxation rates.[6] Furthermore, at low temperature where the relaxation time becomes very long, one observes an initial fast decay of the magnetization (10%–20% of the magnetization) that can be ascribed to spin diffusion effects and was disregarded. After the initial fast recovery a common spin temperature sets in and the long decay rate is a measure of the average relaxation.

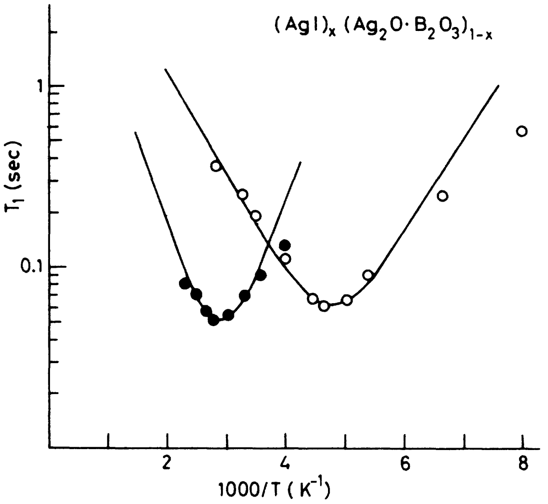

FIG. 1. ^{11}B nuclear spin-lattice-relaxation time T_1 vs 1000/T in two samples of $(AgI)_x(Ag_xO \cdot B_2O_3)_{1-x}$ at $\nu_L = 20$ MHz: (○) for $x = 0.8$ and (●) for $x = 0.2$. The solid lines are the theoretical best fits according to Eq. (3) in the text with the parameters of Table I.

III. RESULTS AND COMPARISON WITH THEORY

The ^{11}B spin-lattice relaxation in borate glass systems is driven by the coupling of the nuclear quadrupole moment $Q = 3.56 \times 10^{-2}$ (10^{-24} cm^2) with the fluctuating electric field gradients (EFG's). For temperatures above about 100 K the dominant mechanism that modulates the EFG at the ^{11}B site is the thermally activated random fluctuations of the BO_4 tetrahedral units among different equilibrium positions. In the samples with $x \neq 0$, containing AgI units, the Ag^+ diffusion could contribute, in principle, to the EFG modulation. However, this relaxation mechanism was shown to be negligible by using both theoretical arguments and experimental verification.[3] At low temperature, when the correlation time associated with the "classical" reorientation of BO_4 units becomes too long to explain the observed relaxation rate one has to invoke as a dominant relaxation mechanism the coupling of the ^{11}B nuclei to the low-frequency disorder modes associated with tunneling in two-level systems (TLS's). In the following, we present and discuss separately the results at high temperatures and those at low temperatures.

A. High-temperature relaxation

Some representative results for the temperature dependence of ^{11}B T_1 in different samples and for different resonance frequencies are shown in Figs. 1 and 2. In all cases a T_1 minimum is observed at temperatures that are a sensitive function of the glass composition. The minimum scales with the resonance frequency according to the BPP-type theory. Thus, an analysis of the high-temperature results in terms of this simple theoretical approach seems justified. If one assumes that the random network of BO_4 groups can undergo reorientational fluctuations among different equilibrium positions with a thermally activated correlation time one can write approximately

$$T_1^{-1} \cong 2W_Q \cong C\left[\frac{\tau}{1+\omega_L^2\tau^2} + \frac{4\tau}{1+4\omega_L^2\tau^2}\right], \tag{3}$$

where ω_L is the Larmor frequency and

$$C = \frac{1}{50}\langle (e^2qQ/\hbar)^2 \rangle = 3.16\langle \nu_Q^2 \rangle$$

is an effective mean-square quadrupole coupling frequency due to the modulation of the ^{11}B EFG among the different positions. By fitting the experimental results with Eq. (3) and by assuming for the correlation time $\tau = \tau_0 \exp(E_A/k_BT)$, one obtains the values for the parameters quoted in Table I. The departure of the experimental points from the theoretical fit on the low-temperature site of the minimum is due to the effect of

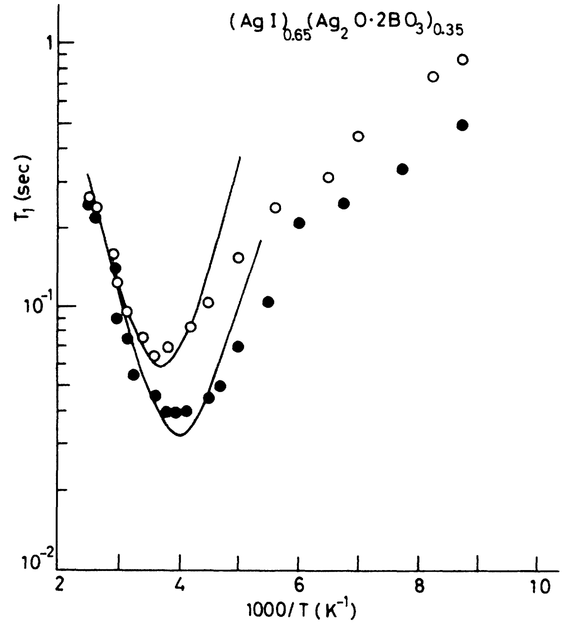

FIG. 2. ^{11}B nuclear spin-lattice-relaxation time T_1 vs 1000/T in a sample of $(AgI)_{0.65}(Ag_2O \cdot 2B_2O_3)_{0.35}$ at two different resonance frequencies: (○) for $\nu_L = 29.6$ MHz and (●) for $\nu_L = 16$ MHz. The solid lines are best fits according to Eq. (3) in the text with the parameters of Table I. Similar results were obtained for $x = 0.0$, 0.2, and 0.5.

TABLE I. Summary of parameters related to ionic diffusion and to local atomic motion in $(\mathrm{AgI})_x(\mathrm{Ag_2O}\cdot n\mathrm{B_2O_3})_{1-x}$ glasses.

Sample		From conductivity	From^{109} Ag NMR		From ^{11}B NMR		
n	x	E_σ (K)	E_A^{Ag} (K)	τ_0 (sec)	E_A^{B} (K)	τ_0 (sec)	$\langle \Delta\nu_Q^2\rangle^{1/2}$ (Hz)
2	0.0						
2	0.2				3500	2×10^{-12}	2×10^{4}
2	0.4	4110[a]	1275[b]	7.3×10^{-10}[b]			
2	0.5				2500	2×10^{-12}	2.2×10^{4}
2	0.55	3360[a]	1043[b]	7.1×10^{-10}[b]			
2	0.65	2860[a]	927[b]	7.8×10^{-10}[b]	2000	2×10^{-12}	2.6×10^{4}
1	0.0						
1	0.2	5000[c]			2200	8.2×10^{-12}	2.3×10^{4}
1	0.5	3800[c]					
1	0.6	3360[c]					
1	0.7	3010[c]					
1	0.8	2300[c]			1330	8.2×10^{-12}	2.1×10^{4}

[a] Reference 2(b).
[b] Reference 26.
[c] Reference 3.

the TLS, as discussed in the following. One can conclude that Eq. (3) even with no distribution of correlation times seems to satisfactorily explain the experimental results, although its validity is known to be only approximate in a solid for a nucleus bearing a quadrupole moment.[11]

B. Low-temperature relaxation

At temperatures below about 100 K the relaxation mechanism described by Eq. (3) becomes totally negligible. The temperature dependence of the ^{11}B relaxation rate is of the form $T_1^{-1} \propto T^{\alpha}$ with α slightly larger than one as shown in Figs. 3 and 4. The preceding quasilinear temperature dependence of the relaxation rate is a well-known general feature of inorganic glasses[12] and is well explained by a variety of models[13-20] for nuclear quadrupole relaxation based on the coupling of the nucleus with the fluctuating EFG associated with the tunneling defects present in amorphous systems constituting the TLS.[4,5] Although the different models have the basic interaction

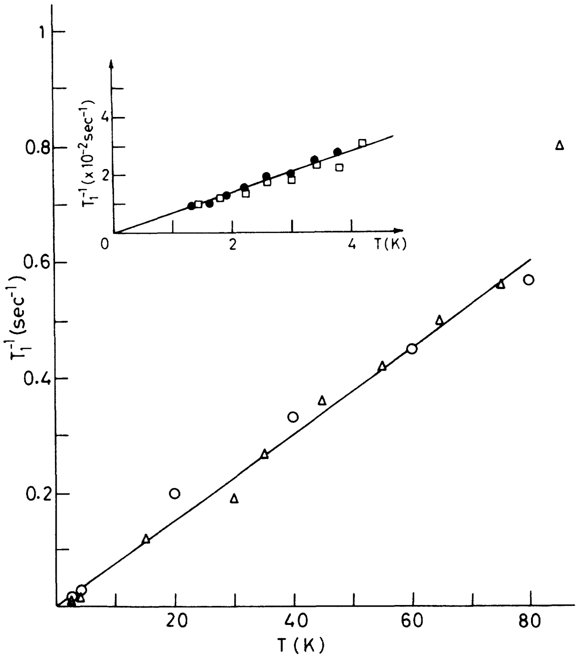

FIG. 3. ^{11}B nuclear spin-lattice-relaxation rate as a function of temperature in $(\mathrm{AgI})_x(\mathrm{Ag_2O}\cdot2\mathrm{B_2O_3})_{1-x}$: (●) and (△) for $x=0.65$ at $\nu_L=10$ and 16 MHz, respectively. (□) and (○) for $x=0.0$ at 10 and 16 MHz, respectively.

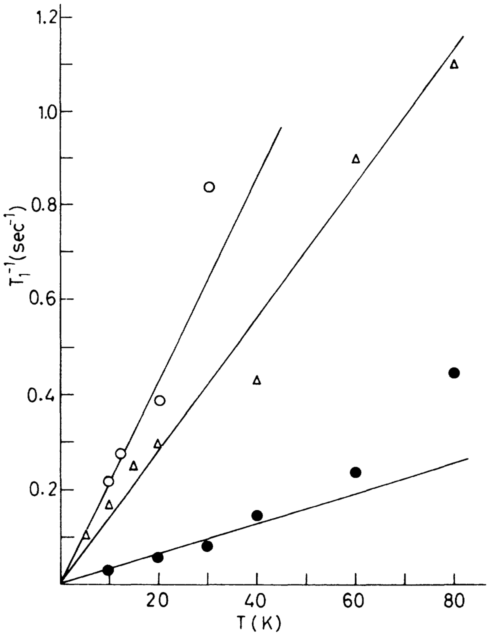

FIG. 4. ^{11}B nuclear spin-lattice-relaxation rate as a function of temperature in $(\mathrm{AgI})_x(\mathrm{Ag_2O}\cdot\mathrm{B_2O_3})_{1-x}$ for different values of the concentration x: (○) for $x=0.2$, (△) for $x=0.5$, and (●) for $x=0.8$. The resonance frequency is $\nu_L=11$ MHz. The straight lines are eye guides.

mechanism in common and lead to similar results regarding the temperature dependence, they differ in the microscopic assumptions. Two basically different approaches can be used. In one of them, the nuclear relaxation is obtained by a Raman process where the nuclear spin flip is accompanied by the contemporary excitation and deexcitation of two nearby coupled disorder modes.[16] In the second approach the tunneling defects are considered as highly nonlinear, localized excitations that induce a large fluctuating EFG on the nuclei contained in an effective sphere around the defect. A semiclassical, weak collision, spectral density approach[21] in the spin-temperature approximations starts from

$$T_1^{-1}=\sum_i \frac{\langle Q^2\rangle |V_i^{(1)}|^2}{\hbar^2} \times \int_{-\infty}^{\infty} \langle \sigma_i(t)\sigma_i(0)\rangle \exp(-\omega_L t)dt \;, \tag{4}$$

where the EFG functions $V_i^{(1)}$ have been expanded in terms of a pseudospin Ising variable σ representing the two possible equilibrium configurations of the ith TLS. The evaluation of the correlation function of $\sigma(t)$ for a pseudospin model of interacting TLS's leads to the expression[6]

$$T_1^{-1}=\langle \Delta\nu_Q^2\rangle \tau_Z \cosh^{-2}\left[\frac{E}{2k_B T}\right] \tag{5}$$

for the nuclear relaxation around a TLS of energy E. The time τ_z is a characteristic time for the fluctuations of the TLS's between the two equilibrium positions. In a pseudospin formalism τ_z can be viewed as a spin-spin relaxation time T_2.[22] In the spin-temperature approximation the relaxation rate for the whole sample is obtained by averaging Eq. (5) with respect to E. The final result valid at low temperature is[6]

$$T_1^{-1} \propto \frac{T^\alpha}{N_{\mathrm{TLS}}} \;, \tag{6}$$

where N_{TLS} is the number density of TLS's, and $\alpha=1$ for a constant density of states $N(E)$. A similar result regarding the temperature dependence is also obtained from the Raman process.[16] In both cases no dependence on the measuring frequency ν_L is predicted.

C. Frequency dependence

At high temperature the ^{11}B relaxation rate depends on measuring frequency as predicted by Eq. (3) for $\omega_L\tau \gg 1$ (see Figs. 1 and 2). On the other hand, at low temperature, where the relaxation rate is dominated by the TLS, the frequency dependence is as shown in Figs. 5 and 6. The data can be best reproduced by a relaxation rate written as the sum of two terms:

$$T_1^{-1}=AT+\frac{BT}{\nu_L^2} \tag{7}$$

with A and B constants that are weakly dependent upon concentration x. As we have seen from Eq. (6), the theoretical predictions based either on a Raman process or on fluctuations of TLS's due to a semiclassical rate

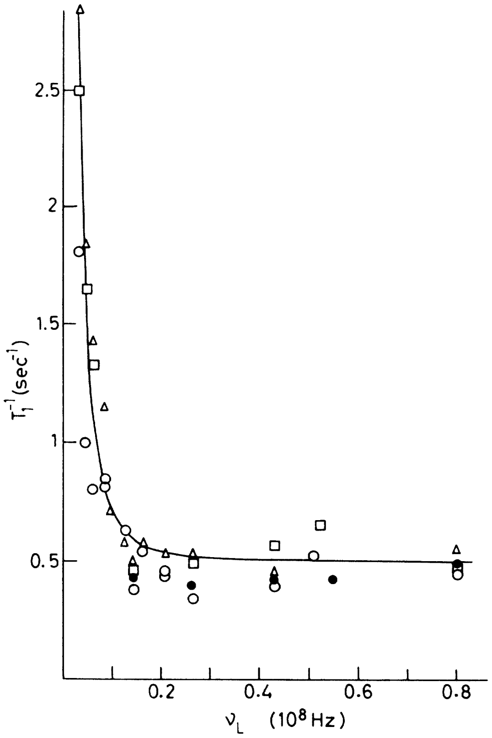

FIG. 5. ^{11}B nuclear spin-lattice-relaxation rate at $T=77$ K, as a function of measuring frequency ν_L in $(\mathrm{AgI})_x(\mathrm{Ag_2O{\cdot}2B_2O_3})_{1-x}$ for different concentrations x: (○) for $x=0.65$, (△) for $x=0.0$, (●) for $x=0.5$, and (□) for $x=0.2$. The solid line represents the behavior of Eq. (7) in the text with $A=6.5\times10^{-3}$ sec^{-1} K^{-1} and $B=2.6\times10^{11}$ sec^{-3} K^{-1}.

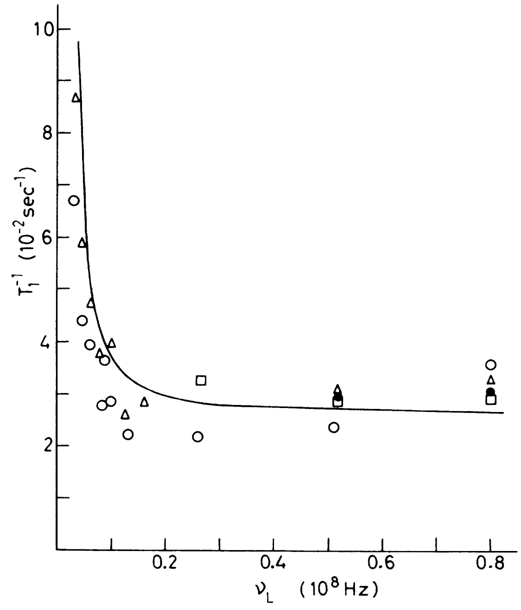

FIG. 6. ^{11}B nuclear spin-lattice-relaxation rate at $T=4.2$ K, as a function of measuring frequency ν_L in $(\mathrm{AgI})_x(\mathrm{Ag_2O{\cdot}2B_2O_3})_{1-x}$ for different concentrations x: (○) for $x=0.65$, (△) for $x=0.0$, (●) for $x=0.5$, and (□) for $x=0.2$. The solid line represents the behavior of Eq. (7) in the text with the same values of the parameters A and B as in Fig. 5.

process do not predict a frequency dependence. A frequency dependence of the power-law type $T_1^{-1} \propto \nu_L^{-\beta}$ is obtained theoretically by introducing in the Raman process a combined mean lifetime of the TLS described by a classical rate process with $\tau = \tau_0 \exp(V/k_B T)$ and assuming V to be the barrier height between the two levels of a TLS.[12] A power-law frequency dependence with $\beta \cong 0-1$ is indeed observed in many inorganic glasses. It should be emphasized that the frequency dependence observed in our experiment [see Eq. (7)] is quite different and cannot be fitted by a power law. In order to interpret the experimental results, let us go back to the relaxation mechanism described in Ref. 6. Equations (5) and (6), which are frequency independent, have been obtained by assuming that the local fluctuations of $\sigma(t)$ are dominated by inter-TLS interactions. Then, the correlation time τ_z in Eq. (5) is a sort of spin-spin relaxation time describing energy conserving mutual pseudospin transitions of two interacting TLS's and it is assumed that $\omega_L \tau_z \ll 1$. However, for isolated or weakly coupled TLS's the spin-spin mechanism should be negligible and the fluctuations should be dominated by the TLS-lattice coupling with the phonon bath. In the tunneling model the fluctuation rate corresponds to a sort of spin-lattice-relaxation time and can be expressed in terms of the parameters of the TLS (Ref. 23)

$$\tau_l^{-1} = \frac{E\Delta^2}{a k_B^3} \coth\left[\frac{E}{2k_B T}\right] , \tag{8}$$

where Δ is the tunnel splitting and $E = (\varepsilon^2 + \Delta^2)^{1/2}$ is the energy difference of the TLS with ε the asymmetry between the two potential minima of the TLS. The constant is

$$a = 2\pi\rho\hbar^4 \bar{v}^5/\gamma^2 k_B^3 \cong 10^{-8}\ \text{sec K}^3 ,$$

where ρ is the mass density, $\bar{v}$ is the mean sound velocity, and γ is the deformation potential that can be determined from thermal conductivity measurements.[24] The expression (8) has its maximum value τ_m^{-1} when $\varepsilon = 0$, i.e., $E = \Delta$. The probability distribution $P(E, \tau_l^{-1})$ for finding a TLS with excitation energy E and relaxation rate $\tau_l^{-1} < \tau_m^{-1}(E)$ turns out to be[23]

$$P(E, \tau_l^{-1}) \cong \frac{n_0}{2\ln(2/u_m)} \frac{\tau_l}{[1 - \tau_m(E)/\tau_l]^{1/2}} , \tag{9}$$

which is strongly peaked in the region of long relaxation times and weakly divergent for the shortest time $\tau_m(E)$, being "U" shaped. The TLS's with the longest relaxation times are those with a high potential barrier separating the two potential minima and consequently a very small tunneling splitting. In the tunneling model, n_0 is the density of TLS's which is assumed constant up to an unspecified maximum excitation energy $E_{\max}$ and $u_m = \Delta_{\min}/E$ is the minimum value of $u = \Delta/E$, which can be taken of the order to 10^{-6}.[22] The tunneling splitting Δ in Eq. (8) is given by $\Delta \cong \hbar\omega \exp(-\lambda)$ with $\lambda \propto d(mV_0)^{1/2}$ where d is the distance between the potential minima, m is the effective mass of the particle, and V_0 is the potential barrier. For reasonable values of the parameters one expects a distribution of Δ values from close to zero up to a maximum value of the order of 0.01–0.1 K. Consequently one has, from Eq. (8), in the hypothesis $E < 2k_B T$, that the fluctuation rate is always smaller than the Larmor frequency ω_L. Thus one expects that a non-negligible number of TLS's exists for which the fluctuation rates are dominated by the spin-phonon mechanism [i.e., τ_l^{-1} given by Eq. (8)] rather than the spin-spin mechanism [see in Eq. (5)]. These slow fluctuating TLS's are expected to give a frequency-dependent term in the nuclear spin-lattice-relaxation rate. This term can be estimated by writing the contribution to the ^{11}B relaxation rate due to the ith slow fluctuating TLS as

$$(T_1^{-1})_i = \langle \Delta\nu_Q^2 \rangle_i \frac{\tau_l(E_i)}{1 + \omega_L^2 \tau_l^2(E_i)} , \tag{10}$$

where $\langle \Delta\nu_Q^2 \rangle_i$ is an effective quadrupole coupling constant that depends on the considered TLS both through the geometric parameters and the value of ε and Δ.[6,25] In the spin-temperature approximation, valid for $T_2 \ll T_1$ the sample can be divided into interaction spheres of mean radius R, inside which the relaxation of all nuclei is due to the fluctuations of EFG tensor caused by the TLS located at the center. The relaxation rate for the nuclei in each sphere can be calculated by averaging over the distance in an isotropic assumption. This can be done by allowing a proper mean volume of radius r_0 to each TLS (formed by one or more boron tetrahedra) and by assuming

$$\langle \Delta\nu_Q^2 \rangle_i = \langle \Delta\nu_Q^2 \rangle_{0i} \quad \text{for } r < r_0 ,$$

$$\langle \Delta\nu_Q^2 \rangle_i = \langle \Delta\nu_Q^2 \rangle_{0i} \frac{r_0^6}{r^6} \quad \text{for } r > r_0 .$$

The result has to be further averaged over the distribution $P(E, \tau_l^{-1})$ of the correlation rates and that of energy E. We assume for the density of states of the TLS $N(E) = n_0 = \text{const}$ between 0 and the cutoff energy $E_{\max}$. By utilizing Eqs. (8)–(10), and considering that for $\Delta < 0.1$ K the condition $\omega_L \tau_l > 1$ is satisfied for excitation energies up to about 10 K, if $T \leq 100$ K, we obtain

$$T_1^{-1} \cong \langle \Delta\nu_Q^2 \rangle_0 \frac{1}{a} \left[\frac{r_0}{R}\right]^3 \left[\frac{\Delta_{\max}}{k_B}\right]^2 \frac{T}{\omega_L^2} , \tag{11}$$

where $(r_0/R)^3$ represents the fraction of the total volume of the sample occupied by the TLS or equivalently the fraction of ^{11}B belonging to the TLS. It should be noted that the average over E also involves the effective quadrupole coupling constant so that $\langle \Delta\nu_Q^2 \rangle_0$ in Eq. (11) is an average value over all TLS's. The contribution derived in Eq. (11) refers only to the isolated, slow fluctuating TLS, and it well describes the experimental behavior of the second term in Eq. (7). The frequency-independent term in Eq. (7) represents the contribution of the fast relaxing TLS. These include both the isolated TLS for which the condition $\omega_L \tau_l > 1$ does not hold and the strongly coupled TLS whose frequency-independent contribution is calculated in Eqs. (5) and (6). It should be noted that the assumption $k_B T > E$ was used in deriving Eq. (11). For very low temperatures ($T < 1$ K) the temperature dependence becomes more pronounced with $T_1^{-1} \propto T^4/\omega_L^2$. This temperature dependence is difficult to observe experimentally since the corresponding contribution to T_1^{-1} becomes negligibly small except for the lowest Larmor frequencies.[25] The values of the constant in Eq. (7) obtained from the data in Figs. 5 and 6 for $(\mathrm{AgI})_x(\mathrm{Ag_2O{\cdot}2B_2O_3})_{1-x}$ and neglecting the small concentration dependence are

$$A = 6.5\times10^{-3} \ , \qquad B = 2.6\times10^{11} \ , \tag{12}$$

A in $\mathrm{sec^{-1}\,K^{-1}}$ and B in $\mathrm{sec^{-3}\,K^{-1}}$. By comparing these values with the theoretical expression (11), one can derive information about the fraction of slow-fluctuating TLS's, as will be shown in the next section.

D. Concentration dependence

The ^{11}B T_1 is only weakly dependent on the concentration x of AgI groups in both glasses with $n = 1$ and 2. Some representative results are shown in Fig. 7. For the glasses with $n = 2$ [Fig. 7(a)] the weak concentration dependence is observed only in the data at low frequency. For the glasses with $n = 1$ the concentration dependence is stronger [Fig. 7(b)] but we do not have the results as a function of resonance frequency. In order to compare the results with the theoretical predictions one should keep the following in mind. At high resonance frequency where the ^{11}B T_1^{-1} is dominated by the fast fluctuating strong interacting TLS, T_1^{-1} is inversely proportional to their density N_{TLS} [see Eq. (6)]. This comes about because $T_1^{-1} \propto \tau_z$ and the fluctuating time τ_z of the interacting TLS goes as $\tau_z \propto (N_{\mathrm{TLS}})^{-1}$. On the other hand, the low-frequency relaxation rate has a non-negligible contribution coming from the isolated slow fluctuating TLS described by Eq. (11). This contribution is proportional to

$$(r_0/R)^3 = (N_{\mathrm{TLS}}^{*} n_B)/N_B \ ,$$

where N_{TLS}^{*} is the density of slow fluctuating TLS, n_B is the number of B atoms inside the TLS covolume and N_B is the density of B atoms in the considered samples. The results in Fig. 7 indicate that there is a weak concentration dependence of the slow fluctuating TLS with a decrease of their number as the concentration of AgI groups increases.

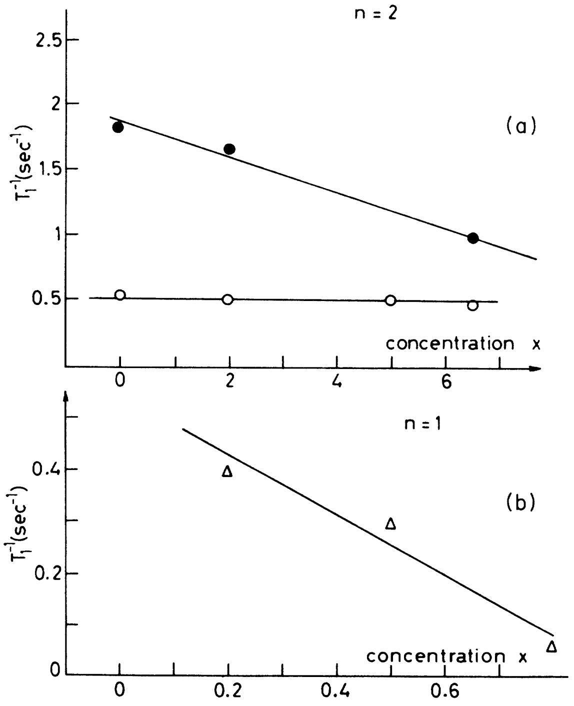

FIG. 7. ^{11}B nuclear spin-lattice-relaxation rate in $(\mathrm{AgI})_x(\mathrm{Ag_2O{\cdot}}n\mathrm{B_2O_3})_{1-x}$ at 4.2 K as a function of concentrations and frequency. In part (a): $n = 2$, (○) for 80 MHz and (●) for 4.4 MHz. In part (b): $n = 1$, (△) for 11 MHz. The straight lines are eye guides.

IV. DISCUSSION AND CONCLUSION

A. High-temperature results

The ^{11}B relaxation rate for $T > 100$ K can be explained reasonably well in terms of a classical BPP-type process. The activated atomic motion that drives the relaxation could be identified as reorientations of the $\mathrm{BO_4}$ groups in agreement with a previous study.[3] The activation energy E_A^{B} for this process is considerably lower than the activation energy E_σ obtained from conductivity measurements (see Table I). The same is true for E_A^{Ag} obtained from ^{109}Ag NMR spin-lattice-relaxation rate measurements,[26] also shown in Table I. The concentration dependence of the three different activation energies is shown in Fig. 8 for the glasses with $n = 2$. It appears quite remarkable that the activation energy E_σ turns out to be the sum of

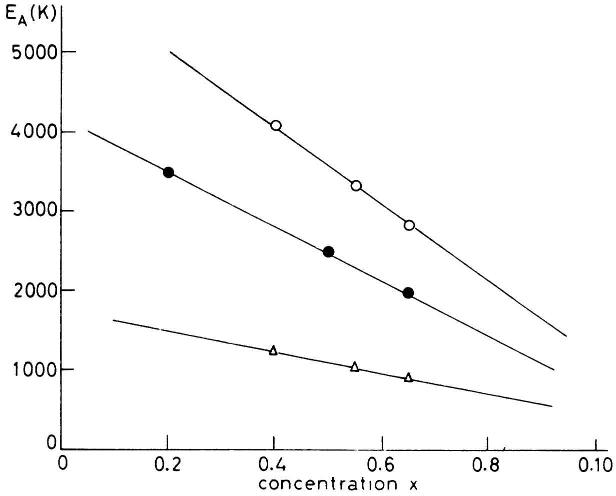

FIG. 8. Activation energies as a function of concentration in $(\mathrm{AgI})_x(\mathrm{Ag_2O{\cdot}2B_2O_3})_{1-x}$. The different values refer to measurements of electric conductivity σ (○), ^{11}B NMR (●), and ^{109}Ag NMR (△) as given in Table I. The straight lines are eye guides.

the activation energies pertinent to the local motion of the Ag and B atoms, respectively,

$$E_\sigma = E_A^{\mathrm{Ag}} + E_A^{\mathrm{B}} \; . \tag{13}$$

This seems to confirm that the activated diffusion of Ag$^+$ ions responsible for the ionic conductivity is the result of a coupling of the local Ag motion with the disorder modes of the BO$_4$ groups as already suggested.[3] A recent model[27] proposes a relationship between E_σ and the hopping activation energy E_A for the diffusing ion, $E_\sigma / E_A = 1/(1-n)$, where $n (0 < n < 1)$ is the phenomenological exponent characterizing the frequency dependence of the ac conductivity at high frequencies, i.e., $\sigma(\omega) \propto \omega^n$. This relation is ascribed, in the preceding model, to a coupling of the diffusing ions with the thermal bath. It is interesting to point out that if one assumes the thermal bath for the diffusing silver ions as mainly due to the BO$_4$ motion the relation (13), together with $E_A^{\mathrm{Ag}} / E_\sigma = 1 - n$, implies $E_A^{\mathrm{B}} / E_\sigma = n \cong 0.7$ (see Fig. 8 and Table I), which is close to the average experimental value for borate ionic glassy conductors.[28,29] However, this comparison should be considered with some caution since n seems to be slightly temperature dependent.

B. Low-temperature results

At temperatures below 100 K the ^{11}B relaxation rate is dominated by the dynamics of the TLS. While the observed linear temperature dependence of T_1^{-1} is a confirmation of a result found in most glassy materials, the frequency dependence observed here (see Fig. 5) seems peculiar of the systems investigated and it was not observed before. The results can be explained by assuming that two types of TLS's are present: TLS's that are strongly coupled among themselves and give rise to fluctuations of the EFG with a characteristic time $\tau_z \ll \omega_L^{-1}$ and isolated TLS's with $\tau_l \gg \omega_L^{-1}$. The fraction of such slow fluctuating TLS's can be estimated by comparing Eq. (11) and the experimental values in Eq. (12). One has

$$B = \frac{\langle \Delta \nu_Q^2 \rangle_0}{(2\pi)^2} \frac{1}{a} \left[\frac{r_0}{R} \right]^3 \left[\frac{\Delta_{\max}}{k_B} \right]^2$$
$$= 2.6 \times 10^{11} \ \mathrm{sec}^{-3} \mathrm{K}^{-1} \; .$$

By choosing

$$\langle \Delta \nu_Q^2 \rangle / (2\pi)^2 \cong 4 \times 10^8 \mathrm{Hz}^2 \; ,$$

as in the high-temperature relaxation (see Table I), $a \cong 10^{-8}$ sec K^3, as obtained from thermal conductivity measurements[24] one has

$$\left[\frac{r_0}{R} \right]^3 = \frac{N^*_{\mathrm{TLS}} * n_B}{N_B} = \frac{6.5 \times 10^{-6}}{(\Delta / k_B)^2} \; , \tag{14}$$

where n_B, N_B, and N^*_{TLS} are defined in Sec. III D. From the linear term in the specific heat[7] one can obtain an estimate of the constant density of states $N(E) \cong n_0$ for all kinds of TLS's (Ref. 5),

$$C_V \cong \frac{\pi^2}{6} k_B^2 n_0 T \; . \tag{15}$$

From the experimental results,[7] one has for the glasses with $n = 2$, averaging for all x values, $N(E) = n_0 \cong 1.410^{41}$ J^{-1} cm^{-3}. The total density of the TLS is

$$N_{\mathrm{TLS}} = n_0 E_{\max} = 1.9 \times 10^{18} \left[\frac{E_{\max}}{k_B} \right] \; . \tag{16}$$

The fraction of slow-relaxing TLS's can be written [from Eqs. (14) and (16)]

$$f = \frac{N^*_{\mathrm{TLS}}}{N_{\mathrm{TLS}}} \cong \frac{7 \times 10^{-2}}{n_B} \frac{k_B^3}{\Delta_{\max}^2 E_{\max}} \; , \tag{17}$$

where we have used $N_B = 2 \times 10^{22}$ cm^{-3} for the average density number of B atoms in our samples.[7] Since there are no independent measurements of n_B, $\Delta_{\max}$, and $E_{\max}$, in Eq. (17), one can only check the consistency of these results by making reasonable assumptions. For $\Delta_{\max} = 0.05$ K and $E_{\max} = 10$ K, one has $f = 3/n_B$ and $(r_0/R)^3 = 2.6 \times 10^{-3}$. From specific-heat measurements[7] evidence was found for short-range ordered cluster having a correlation length $\lambda \cong 30$ Å. If one takes λ^3 as the size of the TLS then $n_B = N_B \lambda^3 \cong 500$ and $f = 6 \times 10^{-3}$. The value of n_B should be viewed as an upper limit because it is likely that the dimensionality of the correlated clusters is less than 3.

In conclusion, we may say that the ^{11}B relaxation results give some interesting insights into the microscopic origin of the disorder modes. At high temperature both the BO$_4$ and the AgI groups undergo local motions. The concomitant thermal excitation of both these degrees of freedom seems to be necessary to produce the hopping diffusion of the Ag$^+$ ions.

At low temperature one finds that a fraction of TLS's have long relaxation times and give rise to a frequency-dependent term in the spin-lattice-relaxation rate. These TLS's could be identified as groups of many BO$_4$ tetrahedral units that undergo cooperatively, phonon-assisted tunneling motion with tunneling splitting up to 0.1 K, implying an energy barrier much lower than the energy barrier of about 2000–3000 K associated with the local motion of a single BO$_4$ group. The hypothesis of the existence[30] of two types of TLS's receives new support from these results. It should be noted that the TLS's just described are consistent with the specific-heat results,[7] which indicate the presence of strongly anharmonic local motion in correlated regions that could be identified as the TLS.

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