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A new problem in the correlation of nuclear-spin relaxation and ionic conductivity in superionic glasses

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Abstract

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Keywords

glasses, activation energies, ionic conduction, conducting polymers, electrolytes

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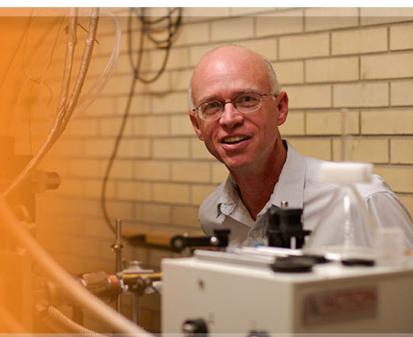
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A new problem in the correlation of nuclear-spin relaxation and ionic conductivity in superionic glasses

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Following the recent resolution of the longstanding problem of reconciling constant frequency nuclear-spin lattice relaxation (SLR) activation energies and d.c. conductivity activity energies in ion conducting glasses, we point out a new problem which seems not to have been discussed previously. We report conductivity data measured at a series of fixed frequencies and variable temperatures on a lithium chloroborate glass and compare them with SLR data on identically prepared samples, also using different fixed frequencies. While phenomenological similarities due to comparable departures from exponential relaxation are found in each case, pronounced differences in the most probable relaxation times themselves are observed. The conductivity relaxation at 500 K occurs on a time scale shorter by some 2 orders of magnitude than the ^7Li SLR correlation, and has a significantly lower activation energy. We show from a literature review that this distinction is a common but unreported finding for highly decoupled (fast-ion conducting) systems, and that an inverse relationship is found in supercoupled salt/polymer "solid" electrolytes. In fast-ion conducting glasses, the slower SLR process would imply special features in the fast-ion motion which permit spin correlations to survive many more successive ion displacements than previously expected. It is conjectured that the SLR in superionic glasses depends on the existence of a class of low-lying traps infrequently visited by migrating ions.

I. INTRODUCTION

The failure of the classical Blombergen, Purcell, and Pound (BPP) theory to describe nuclear-spin lattice relaxation (SLR) in ionically-conducting glasses,¹⁻⁴ and the need for a nonexponential relaxation assumption to provide accord with experiment,⁵⁻⁸ has been known for a long time. However, although Ngai⁵ recognized that relationships between SLR and conductivity anomalies were to be expected, it has only recently been pointed out⁹⁻¹¹ that the longstanding discrepancy between activation energies for dc cationic conductivity and for SLR for the same cation in the same glass can be the direct and artificial consequence of the nonexponential nature of the relaxation. It is a simple consequence of the facts that (i) nonexponential relaxation leads to frequency-dependent conductivity,⁵ and also frequency-dependent SLR for frequencies above that of the system's internal relaxation frequency; (ii) in the frequency-dependent range, the isochronal (constant frequency) activation energy is smaller than the dc value by a factor which depends largely on the nonexponentiality factor. The more nonexponential the relaxation, the greater the difference. The origin of the difference in dc conductivity activation energy and the usual ~ 10 – 100 MHz SLR activation energy is then primarily a consequence of the fact that almost all of the early SLR data were acquired in the frequency-dependent (ac) range (in consequence of

the low intrinsic relaxation frequencies for most glasses), while the conductivity measurements, made using lower frequency admittance bridges,⁹ were easily observing the dc behavior. To support this view, measurements conducted isochronally at frequencies approaching those of the SLR measurement were shown to give results qualitatively comparable to those of SLR, viz., both lower activation energies and unphysically low preexponents.⁸⁻¹¹

Since that time, a number of studies¹²⁻¹⁷ have been conducted on glassy systems with maximally decoupled cations in which the internal relaxation frequency rises *above* the SLR spectrometer frequency well before the glass transition temperature is reached, thus exposing the frequency-independent SLR regime for study. Ideally, such measurements should be performed on the same sample—one that has been initially characterized by the more versatile ac conductivity technique. Ribes and co-workers¹² and Martin *et al.*¹³ have recently reported such studies for the system $\text{Li}_2\text{S}-\text{SiS}_2$ at several compositions, while Borjesson and colleagues^{14,15} have done similar work on the more difficult, but even more decoupled ^{109}Ag nucleus in the $(\text{AgI})_{0.6} \cdot (\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3)_{0.4}$ glass. This latter system had the advantage that a mechanical relaxation at frequencies even higher than that of the SLR spectrometer had previously been characterized using Brillouin scattering¹⁸ to identify the temperature at which the phonon damping due to Ag^+ jumping was maximized.

These studies¹²⁻¹⁷ all reported that, when viewed in the expanded temperature-frequency field, a pleasing degree of

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accord between SLR and conductivity phenomenologies was obtained. For instance, Martin *et al.*¹³ reported that the high-temperature (dc) T_1 activation energy was now consistent with the dc conductivity energy, while Niklasson and Borjesson,¹⁵ by analyzing the high-frequency conductivity using power-law fits, rather than the previous^{13,19,20} modulus formalism, found agreement between the spectral densities, or correlation functions, for conductivity and SLR.²¹ Elliott²² has since constructed a microscopic theory for the SLR based on the assumption that the correlation function for the fluctuations involved in SLR is identical with that used in his diffusion-controlled-relaxation model for ionic conductivity²³ (a development of the original one-dimensional Glarum model for dielectric relaxation). Unless the diffusion-independent term in Elliott's model is important, the characteristic times for conductivity (or dielectric) relaxation and SLR should then have the same temperature dependence—both being controlled by the arrival of a diffusing ion at the site of a "defect" or relaxable subunit—and should have comparable magnitudes.

The aim of this paper is to show that, in a favorable case, the relation of SLR to conductivity is not so clear cut. The case is that of Li^+ motion in a $\text{LiCl-Li}_2\text{O-B}_2\text{O}_3$ glass in which the Li^+ motions are so free from the matrix that their jumping frequency can cause maximum damping of 30 GHz acoustic phonons, i.e., $\omega\tau \approx 1$, more than 100 K below T_g (Ref. 24) (as for the $\text{AgI-Ag}_2\text{O-B}_2\text{O}_3$ case mentioned earlier). In such a case, the T_1 minimum for a ~ 30 MHz SLR experiment would be expected far below T_g , but this has not been borne out in the recent experimental study of Martin *et al.*¹⁷ We show, using samples identical to those provided by one of us (M.T.) for Martin *et al.*'s SLR study, that the conductivity relaxation time (which is close to the mechanical relaxation time) is some 2 orders of magnitude shorter than the SLR correlation time. Furthermore, we will show that the activation energies are significantly different. These findings, coupled with the additional recent observation²⁵ that the kinetics of a process as complicated as crack nucleation and failure in glass fibers from the same system, match with the kinetics of the conductivity, suggest that there is something yet to be understood about SLR in ionic glasses. Our observations will then be used as a basis for reexamining the conductivity/SLR relations of other recent studies.

II. EXPERIMENT

Starting materials were reagent-grade LiCl (Mallinckrodt), Li_2CO_3 (Fisher), and B_2O_3 (99.9% from Apache Chemicals). LiCl and B_2O_3 were vacuum dried at about 100°C for several days before use. The ground and mixed materials were heated in a platinum crucible with cover at temperatures between 700 and 850°C for 1 h and then melted at $\sim 960^\circ\text{C}$ for 15 min. The very fluid melt was poured onto a stainless-steel plate and pressed quickly to a thickness of about 0.5 mm using a second plate. The quenched samples were then annealed at 320°C for 10 h in a dry He atmosphere. The glass obtained was slightly colored, presumably due to traces of Pt^{2+} from the Pt cruci-

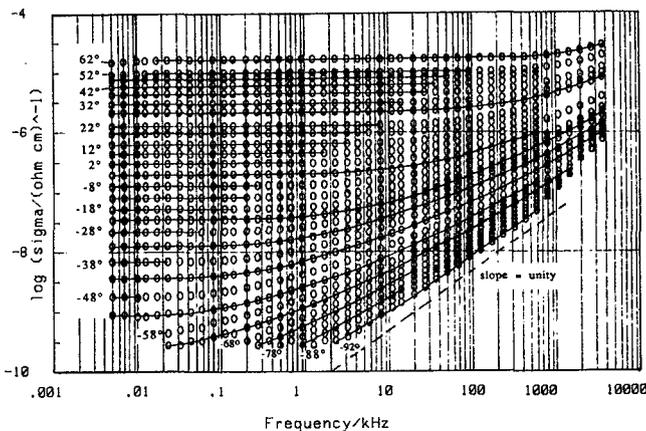


FIG. 1. Conductivity as a function of frequency on log-log plot for the chloroborate glass $0.6\text{LiCl-}0.7\text{Li}_2\text{O-}1.0\text{B}_2\text{O}_3$, at 5 K intervals. The temperature of measurement is indicated on the left of selected isotherms.

ble. This was assumed to have negligible effect on the conductivity. The composition studied was $(\text{LiCl})_{0.6}(\text{Li}_2\text{O})_{0.7}(\text{B}_2\text{O}_3)_{1.0}$, this being chosen after the higher LiCl content composition studied successfully by Borjesson²⁴ proved difficult to measure reproducibly.

Taking precautions to protect the sample from moisture-induced surface deterioration, gold electrodes were sputtered onto the disc samples using a ring mask to provide a well-defined electrode dimension. The cell constant, 0.0559 cm^{-1} , was determined by micrometer determination of the disc thickness (to $\pm 0.002\text{ cm}$) and knowledge of the diameter of the smaller gold electrode. The sample was then mounted in a sealed metal cell in which it was suspended between spring-loaded contacts, and the conductivity and capacitance were determined over the frequency range $8\text{ Hz-}4 \times 10^6\text{ Hz}$ using a Hewlett Packard model 4192 A frequency analyzer. The temperature range covered by the measurements was -88°C to $+62^\circ\text{C}$, though here we use a restricted sample of the results in the analysis to avoid any errors due to lead impedances and capacitances at high frequencies or from measurements made too near the bridge high impedance limits. The temperature was measured using a Cr-Al thermocouple in close contact with the sample inside the sealed cell. The whole assembly was mounted in a temperature smoothing controlled to $\pm 0.02\text{ K}$ by a Eurotherm temperature controller. The whole data-taking process was automated as described in Ref. 26. The glass transition temperature was determined using a Perkin Elmer DSC-4 at 10 K/min .

III. RESULTS

The data are presented in the usual form of $\log\sigma(f)$ vs. f for various isotherms in Fig. 1. Figure 2 shows a reduced set of these data in the same form and as transposed to the less common isochronal (constant probe frequency) Arrhenius plot form, in order to show their relationship. The dashed and dotted lines are explained later.

Finally, we present in Fig. 3 the combined conductivity and capacitance data in the complex electrical modulus form, since the M'' peak frequencies allow us to define the

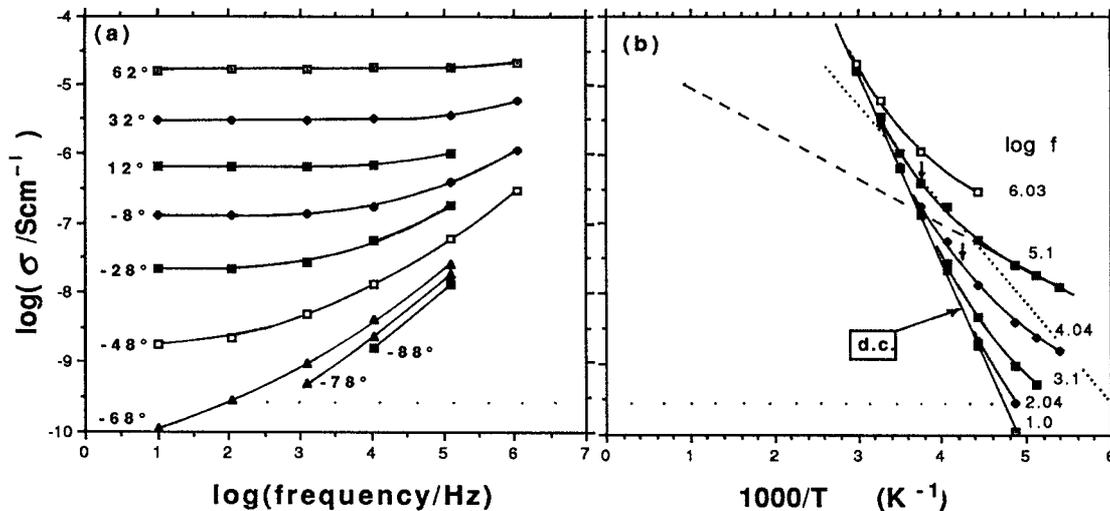


FIG. 2. (a) Selection of data from Fig. 1 shown in relation to Arrhenius plots of the same data (b). Dotted line shows slope expected from Eq. (1). Arrows indicate points of departure of data from Eq. (2), see Fig. 3.

conductivity relaxation times, we need to compare with those for SLR. For clarity, the real part of the modulus M' is not shown. It rises to the value 0.07 at 10^6 Hz in the manner seen in many previous cases.¹⁹ This value corresponds to a high-frequency dielectric constant " ϵ_∞ " of 14 at the lowest temperature of the study, although a limiting low value of ϵ_∞ has not been reached even at 10^6 Hz and -62°C .

IV. DISCUSSION

The isochronal Arrhenius plots of Fig. 2 again confirm the lower activation energies yielded by constant frequency measurements of relaxation processes under $\omega\tau > 1$ conditions. However, the "activation energy" in the ac ($\omega\tau > 1$) regime does not accord well with the SLR low-temperature ($\omega\tau > 1$) regime activation energy, even with our conser-

vative data set. Since the SLR activation energy has been found for many glasses⁸ to be related to the d.c. conduction activation energy by the simple expression

$$E_a(\omega\tau > 1) = \beta E_{a(\text{d.c.})}, \quad (1)$$

where β is the parameter which measures the departure of conductivity relaxation from exponentiality in the Kohlrausch-Williams-Watts (KWW) approximation

$$\theta_{(t)} = \exp[-(t/\tau)^\beta], \quad (2)$$

this is a matter for some concern.²⁷ The pattern we see, one of curvilinear a.c. plots with average Arrhenius slopes that decrease with increasing frequency, is one common to previous studies.^{9-13,27} While the difference at the highest frequencies and lowest temperatures in some studies may in part be due to measurement inaccuracies in these conditions, its continued presence in the more reliable mid-frequency ranges suggests real differences between the conductivity and SLR response functions. Master plots of conductivity M'' spectra of superionic glasses always show positive deviations from the transformed KWW function at or above half height (see Fig. 3 and Refs. 20 and 28), so the source of the deviation from Eq. (1) in the case of conductivity can be assigned to the onset of the excess loss mechanisms. This is also implied in a recent discussion by Jain *et al.*²⁷ The point at which these should begin to influence the slope of the a.c. conductivity is marked by an arrow on selected isochrones in Fig. 2(b), and is seen to be quite close to the point of departure from the d.c. conductivity line. These additional mechanisms, which anticipate the transition to the limiting high-frequency $\sigma \sim f^\alpha$ ($\alpha > 1$) regime,⁹ evidently do not affect the SLR response, at least not at $\omega\tau$ values as close to 1.0 as in the case of conductivity. In this respect, the SLR response behaves more like that of conductivity in poorly conducting glasses (low decoupling indexes) in which the conformity to the transformed KWW function extends over a wider $\omega\tau$ range.

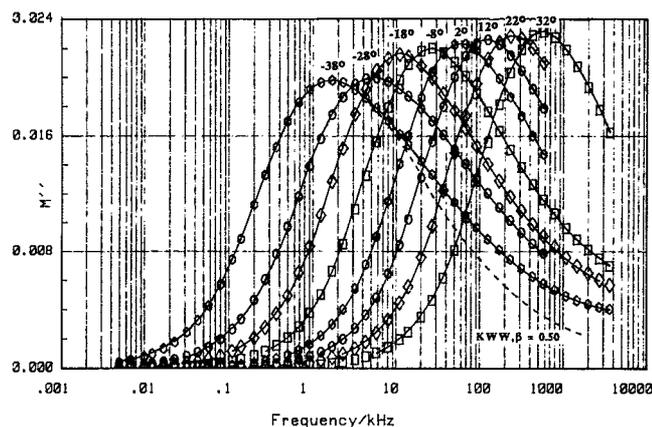


FIG. 3. Imaginary part of the electrical modulus obtained from conductivity data of Fig. 1 and capacitance data (obtained simultaneously) at various temperatures. The frequency at the peak of the modulus plot defines the conductivity relaxation time via Eq. (3). The dashed line is a plot of M'' for the case in which the Fourier transformed KWW function [Eq. (2)] is correct at all frequencies.

This is, in fact, quite consistent with the main point of this paper to which we now turn attention.

Rather than focusing attention on the ac "activation energies," we now examine the relationship between the actual characteristic times, τ_σ , for the two processes. These are determined from the conditions under which maximum coupling between the fixed frequency probe field (ω_p) and the relaxing system occurs, using the general relation $\omega_p \tau_c \approx 1$ [in the particular case of SLR, it is more accurate to write $\omega \tau \approx 0.6$ for the maximum (but still very weak) coupling condition in BPP theory, but the effect of this refinement is negligible compared with the differences in characteristic times we will be discussing].

For the SLR process, this condition is signaled by arrival at a minimum value of the spin-lattice relaxation time T_1 . At the T_1 minimum $\omega_L \tau_c \approx 1$, where ω_L is the Larmor frequency in radians s^{-1} for the chosen magnetic field. For conductivity, this condition is defined by the arrival at a maximum value of M'' (Fig. 3), and we obtain a characteristic time τ_σ from the relation

$$\tau_\sigma = (2\pi f_{\max})^{-1}. \quad (3)$$

Under conditions in which the maximum cannot be observed, an average conductivity relaxation time can be obtained¹⁹ from the d.c. conductivity using the Maxwell-like relation

$$\langle \tau_\sigma \rangle = \frac{\epsilon_0 \epsilon_\infty}{\sigma_{d.c.}} \quad (4)$$

in which ϵ_0 is the permittivity of free space and ϵ_∞ is 14 (see Sec. III).

Because the modulus analysis suppresses electrode capacitance effects, τ_σ and $\langle \tau_\sigma \rangle$ defined in these ways are always in close agreement [c.f. comparisons of Eq. (4) values with those made using $\tan \delta$ maxima],²⁹ although small differences must be expected because of the relationship²⁸

$$\langle \tau_\sigma \rangle = \frac{\tau_\sigma \Gamma(1/\beta)}{\beta}, \quad (5)$$

where Γ is the gamma function and β is the nonexponentiality parameter of the "universal" KWW function, Eq.(2). For β values of 0.64 and 0.5, the differences amount to 0.1 and 0.3 log units, respectively.²⁸

We will use this treatment of the conductivity data in an initial comparison with the SLR results of Martin *et al.*¹⁷ but it should be recognized here that there is currently an increasing interest and persuasion³⁰⁻³² in a return to the conventional treatment of electrical relaxation in glasses in which the glass is treated as a relaxing dielectric with a dc conductance in parallel. This alternative data treatment will be considered as part of the later discussion.

The conductivity relaxation times obtained from the M'' peak frequencies (τ_σ), and from dc conductivities ($\langle \tau_\sigma \rangle$), are plotted in Fig. 4 along with the values of τ_c for the SLR process defined from the maxima in $\log(T_1)^{-1}$ vs $1/T$ curves of Ref. 17 for three different spectrometer frequencies. The τ_c values are obtained using the usual assumption that, at the T_1 minimum, the relationship $\omega_L \tau_c$

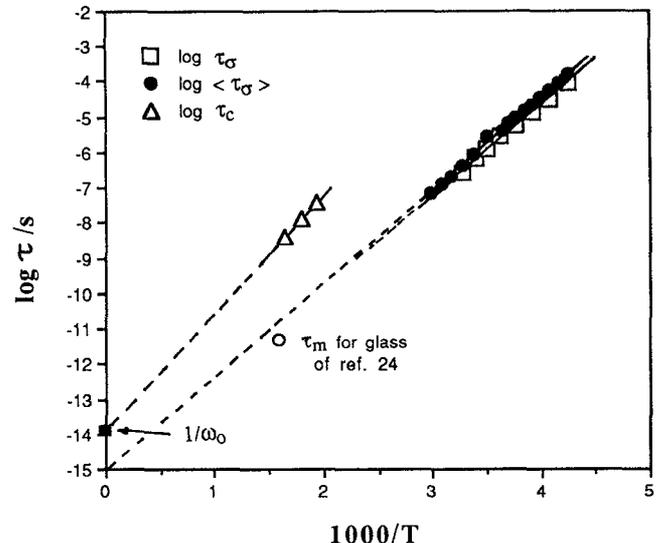


FIG. 4. Conductivity relaxation times, τ_σ and $\langle \tau_\sigma \rangle$ [obtained from M'' plots of Fig. 3, and from dc conductivities using Eq. (4), respectively] compared with ^7Li NMR correlation times obtained from the T_1 minima at different temperatures for different spectrometer frequencies of Trunell *et al.* (Ref. 17). The highest temperature point is more uncertain since the T_1 minimum was barely reached at 40 MHz and was obtained by a short extrapolation based on a T_1 plot at 12.2 MHz. The point designated τ_m is the longitudinal mechanical relaxation time obtained from the 630 K Brillouin linewidth maximum of a lithium chloroborate glass of composition and conductivity very close to that of this study, see Ref. 24. The point marked $1/\omega_0$ was obtained from the far infrared spectrum for a glass of this composition studied in Ref. 46.

≈ 1 holds (where ω_L is the Larmor frequency for the particular spectrometer field). Of course this does not define a unique correlation time any more than does the maximum loss frequency in Fig. 2, since in neither case is the relaxation process exponential. However, if the correlation function is the same or similar for each process, then the characteristic, or most probable time, should differ from the average in the same way. In any case, the difference of τ from the average value $\langle \tau \rangle$ should be small, as seen for τ_σ and $\langle \tau_\sigma \rangle$ in Fig. 4.

It is clear from Fig. 4 that there is a rather large difference between the time scales for the two processes, not only in the value of τ_c at any chosen temperature, but also in the temperature dependences of the two processes. The fact that both processes can be extrapolated to give phononlike τ_0 values^{20,9c} (as indicated by the far IR Li^+ "rattling" time, $1/\omega_0$ in Fig. 4) encourages belief that both sets of measurements are free from artifacts (the conductivity τ_0 is usually^{20,9c} a little shorter than 10^{-14} s). We note additionally the mechanical (longitudinal) relaxation time τ_m obtained by Borjesson²⁴ for a glass of similar composition $(\text{LiCl})_{0.7}(\text{Li}_2\text{O})_{0.7}(\text{B}_2\text{O}_3)_{1.0}$ using an even higher frequency probe than SLR, viz., Brillouin scattering, in Fig. 4. This relaxation time, due to Li^+ ion jumping, accords quite well with the value extrapolated in the present conductivity relaxation study when it is taken into account that the difference is in the direction expected from the higher LiCl content and higher conductivity of Borjesson's glass.

The difference in conductivity and SLR relaxation activation energies seen in Fig. 4 is much larger than the difference ($\Delta E = \frac{1}{2}RT_{av}$) arising from the difference between conductivity and diffusion processes ($\sigma \sim D/T$). This implies that the SLR correlation time is longer mainly because the fluctuation needed to optimize the intrinsically weak relaxation of the spin system is less probable. This could mean that more particles, more or different jumps, or higher degrees of correlation¹⁷ are involved in SLR than in conductivity relaxation. In this respect the observation that, in the cases quoted,¹²⁻¹⁵ the complete T_1 curve requires^{16,17} a greater nonexponentiality parameter for its fitting than does the complete conductivity relaxation curve (M'' spectrum, Fig. 3), would be consistent. However, this cannot be used as an argument supporting different kinetics for the two processes without due consideration (given later) of alternative ways of treating the conductivity/dielectric relaxation. What does seem immediately implicit in Fig. 4 is that the fluctuations (electric field gradient etc.) which couple most effectively to the spin system (hence, which minimize T_1/τ_c) are not those determined by the frequency of ionic jumping unless there is some error in the common view that the conductivity relaxation time and mobile ion jump time are very similar when many ions are present. An obvious question is whether or not there are data on other systems which show the same trend. However, before answering this question, we should first consider a possible source of the discrepancy which would require no revision of the previous expectation of common electrical and SLR correlation functions.

We must ask whether the difference between τ_σ and τ_c could be an artifact of the formalism used to analyze the conductivity relaxation. It could be argued that our complex modulus treatment of the electrical relaxation phenomenon,¹⁹ as opposed to the parallel dc conductor plus dielectric relaxation treatment,³⁰⁻³² causes a distortion of the electrical relaxation which is the origin of the discrepancy. That this possibility does not resolve the discrepancy in time scales is most easily seen from Johari's treatment³⁰ of the phenomenon from the latter standpoint. Rather than subtracting a contribution to the susceptibility due to the dc conductance, Johari attributes the low-frequency part of the modulus spectrum to the dc conductivity and subtracts out a corresponding Lorentzian component. It is clear in this case that the frequency of the maximum in the residual M'' spectrum (which it is argued should give the true dielectric relaxation time) would occur at higher frequencies, corresponding to shorter characteristic times. Thus, in this analysis the difference between electrical (now dielectric) and spin relaxation times would be accentuated rather than removed. We therefore conclude that the relaxation time discrepancy revealed by this study is nontrivial, and turn to the other published works in the area to see if similar differences can be identified.

Of the other studies of Li⁺-containing glasses for which both types of data are available,^{12,13} one¹³ included SLR data at the low frequency of 4 MHz, which is within the common conductance measurement frequency range. An isochronal conductivity scan at 400 KHz (one decade

below the lowest-frequency SLR scan) was published in Ref. 13 and showed a break from the dc curve at 250 K, considerably below the temperature of the T_1 minimum at 4 MHz (345 K) as expected for the lower frequency. However, based on the break temperatures at 40 and 4 KHz, that at 4 MHz (the SLR frequency) would also occur at a lower temperature, 300 K, than for the SLR T_1 minimum. This implies that conductivity relaxation is the faster process since conductivity is evidently able to follow the field oscillations to lower temperatures. The direct comparison is made as before by using the dc conductivities to calculate the conductivity relaxation time, via Eq. (2), at the temperature of the T_1 minimum. This requires a short extrapolation of the dc conductivity data available in Ref. 13. The result is $\langle\tau_\sigma\rangle = 10^{-9.7}$ s—more than 2 orders of magnitude shorter than the ⁷Li τ_c value ($1/\omega_L = 10^{-7.4}$ s). Since this study, like that¹⁷ with which we make comparison in the present paper, was performed at several frequencies, we can compare the activation energies of τ_σ and τ_c . As in Fig. 4, that for SLR proves to be considerably larger, suggesting that our observation is general. It should be noted here that the T_1 findings of Martin *et al.*¹³ are well supported by the single-frequency study of Pradel *et al.*¹⁶ The latter authors analyzed their data using a Davidson–Cole relaxation function and found both the spectral width parameter $\alpha_{DC} = 0.3$, and the E_σ to be greater than for dc conductivity.

Turning to ¹⁰⁹Ag relaxation, we note that in Ref. 14 a difference between τ_c and other relaxation times associated with Ag⁺ motion in (AgI)_{0.6}(Ag₂O·2B₂O₃)_{0.4} was recognized, but the difference was only cited as evidence for the failure of BPP theory for SLR. If we quantify the τ_σ vs τ_c difference, we find τ_c for ¹⁰⁹Ag (obtained from 12.5 MHz studies) is $10^{-7.8}$ s at the T_1 minimum (308 K) and this is 1.5 orders of magnitude longer than the value $10^{-9.3}$ s for conductivity relaxation at the same temperature.²⁰ Although smaller than in the previous case, this is still a large difference, especially in view of the fact that the longitudinal mechanical relaxation time interpolated from Brillouin scattering¹⁸ and ultrasonic data³³ agrees with the conductivity relaxation time within 0.1 orders of magnitude at this temperature.

The remaining ¹⁰⁹Ag study is that of Roos *et al.*¹⁶ on (AgI)_x(Ag₂S·GeS₂)_{1-x} glasses which were characterized electrically by Pradel and Ribes.³⁴ The SLR correlation time for the glass of $x=0.5$ is $10^{-7.8}$ s at 282.5 K compared with $10^{-10.0}$ for $\langle\tau_\sigma\rangle$ at the same temperature. This discrepancy is comparable to that found by Chung *et al.*¹⁴ Roos *et al.* found that the Davidson–Cole distribution function was incapable of giving a satisfying fit to the $\log(T_1)^{-1}$ vs $1/T$ plot, hence, gave no DC parameters which could be compared with those for the conductivity relaxation.

From the aforementioned review, it would appear that the τ_c vs τ_σ gap to which we have drawn attention is real and general. Its resolution should provide additional insights into mechanisms of, and cooperative effects in, ionic transport processes in glasses and supercooled liquids.

In seeking to clarify this problem, it would be helpful to pursue joint conductivity/SLR studies into the viscous

liquid state above T_g to see to what extent the differences we have identified disappear as the conductivity and structural relaxation times approach each other.⁸ One case is already available since one of the first systems ever characterized with respect to conductivity relaxation, LiCl-H₂O, has recently³⁵ been studied by both conventional (⁷Li) and β -radiation detected (⁸Li) NMR techniques. Comparing the latter studies on LiCl·4D₂O with short extrapolations (to the same composition) of conductivity relaxation data on LiCl-H₂O solutions, we find that the ⁷Li SLR relaxation time and the conductivity relaxation time are the same within 10^{0.1}.³⁶ This seems consistent with the pattern we have unfolded because in the LiCl-H₂O system it was shown³⁷ that the decoupling index above T_g was close to unity implying that conducting and matrix species relax on the same time scale. For fast-ion glass systems such coincidence of time scales is only approached as $T \rightarrow \infty$ in the liquid state.

Such consistency suggests we should look for a case in which the decoupling index is in the inverse sense, i.e., in which the conductivity relaxation is slower than the matrix relaxation. Although such a system cannot easily be studied in the glassy state, its liquid-state behavior could be expected to show the opposite relation of NMR correlation times and conductivity relaxation times to that observed for superionic glasses. A suitable case in which supercoupling of conducting modes to matrix modes has been demonstrated³⁸⁻⁴⁰ is the salt-in-polymer type of "solid" electrolyte, in which it would indeed appear that the SLR effective fluctuations occur on shorter time scales than does conductivity relaxation. This has been noted without quantification by Greenbaum *et al.*⁴¹ and data provided by these workers suggest that the differences in τ_σ and τ_c are of the order of 10^{0.7}. Whether or not there are any differences in the temperature dependence in this case cannot be determined at this time. However, the inversion of the τ_c/τ_σ ratio, under the same circumstances that the τ_s/τ_σ ratio (i.e., the decoupling index,⁹ τ_s is the structural relaxation time) inverts, provides a coherent pattern which we believe deserves further quantitative exploration.

We conclude with further consideration of the origin of the difference between τ_c and τ_σ in these systems since the explanation is necessarily of interest in connection with migration mechanisms. We invoke two scenarios. The first attributes the difference to correlation effects and the second to site distinction effects.

First, let us suppose that the Li⁺ ion hops do not occur randomly but rather are highly correlated through the long range Coulomb interaction (because of the need to maintain overall electrical neutrality with the immobile anion network). Then the effect of individual ion hops on the damping of the excess nuclear spin energy should be diminished because the correlations serve to smooth out the field gradient differences between different sites. Thus, instead of the damping maximum time scale corresponding to the ion jump time scale, it may be longer by an amount which reflects the efficiency of the interaction coupling. It seems reasonable to suppose that the correlations will become stronger the lower the temperature, hence the differ-

ence between τ_σ (reflecting individual jumps) and τ_c (reflecting correlation-corrected jumps) could increase with decreasing temperature, as observed.

On the other hand, one could argue that the larger activation energy for τ_c implies the presence of a distinct class of deep traps in which the electric field gradient and/or the dipolar interactions which couple to the spin system are very different from those in the shallower traps in which the ions must spend most of their time. To understand the domination of conductivity by shallow-trapped ions, one must suppose the shallow traps to be highly degenerate. Because of the field gradient/dipolar effect, however, the less frequent visits to the deeper traps would dominate the SLR. An increase in shallow trap depth in poorer conducting glasses would explain the tentative correlation of τ_c/τ_σ with R_T .

This latter picture has much in common with that underlying the weak electrolyte model.⁴² The emphasis on a trapping topology we invoke here over the more common energy landscape picture of ion migration, however, implies an analogy with models of electron transport in glasses⁴³ and helps to rationalize their common features.⁴⁴ To broaden the picture even further, we should add that if studies in the liquid state of moderately fast-ion conductors can show that τ_c varies in a non-Arrhenius fashion with changing temperature so as to approach both τ_σ and τ_s at high temperature, then the phenomenon to which we have drawn attention would be identified as another participant in the serial decoupling phenomenon discussed recently by several authors.⁴⁵

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