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# AC and DC Studies of Non-Exponential Relaxation Processes in Superionic Conductors: Correlation of Conductivity and NMR Studies

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## **Abstract**

This paper considers the results of NMR relaxation studies of fast ion glasses in the light of variable frequency electrical conductivity measurements. We show that the low activation energy observed for relaxation processes studied at constant frequency below the temperature of the  $T_1$  minimum is reproduced by the corresponding constant frequency conductivity measurements. Other characteristics of the constant frequency conductivity in this low activation energy regime, such as the unphysically low pre-exponent, match with the corresponding observations for NMR measurements. Since the activation energy observed at constant frequency in the frequency-dependent regime for conductivity depends on the characteristic departure from exponential relaxation for the conductivity process, we conclude that the NMR activation energy is likewise a simple consequence of the nonexponential character of ionic relaxation in the glass. In this case, the low activation energy attributed to processes probed by NMR relaxation is simply a misinterpretation since it is found, in the wide frequency range studies available to admittance bridge measurements, that all elements of the relaxation spectrum have essentially equal activation energies.

## **Disciplines**

Ceramic Materials | Semiconductor and Optical Materials

## **Comments**

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## AC AND DC STUDIES OF NON-EXPONENTIAL RELAXATION PROCESSES IN SUPERIONIC CONDUCTORS: CORRELATION OF CONDUCTIVITY AND NMR STUDIES

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### ABSTRACT

This paper considers the results of NMR relaxation studies of fast ion glasses in the light of variable frequency electrical conductivity measurements. We show that the low activation energy observed for relaxation processes studied at constant frequency below the temperature of the  $T_1$  minimum is reproduced by the corresponding constant frequency conductivity measurements. Other characteristics of the constant frequency conductivity in this low activation energy regime, such as the unphysically low pre-exponent, match with the corresponding observations for NMR measurements. Since the activation energy observed at constant frequency in the frequency-dependent regime for conductivity depends on the characteristic departure from exponential relaxation for the conductivity process, we conclude that the NMR activation energy is likewise a simple consequence of the nonexponential character of ionic relaxation in the glass. In this case, the low activation energy attributed to processes probed by NMR relaxation is simply a misinterpretation since it is found, in the wide frequency range studies available to admittance bridge measurements, that all elements of the relaxation spectrum have essentially equal activation energies.

### INTRODUCTION

Although much use of variable frequency bridges has been made in the study of fast ion conduction in glasses, the variable frequency has been employed principally for the purpose of extrapolating out effects of imperfect electrode surface contacts. It has only infrequently been used to study basic aspects of the bulk conductivity process.<sup>(1-4)</sup> The results of such measurements are almost never presented in the form of Arrhenius plots for a constant frequency measurement, and partly for this reason the phenomenological connection to the sometimes confusing results obtained from NMR relaxation studies (which are always conducted at constant spectrometer frequency) has, until two years ago<sup>5,6,7)</sup> gone unnoticed. The purpose of this paper is to present conductivity data in the latter form, interpret them in the light of the considerable understanding<sup>(1)</sup> of frequency-dependent electrical conductivity phenomena, and thereby to clarify the meaning of the NMR measurements.

The parallels between a.c. conductivity and NMR results which we will demonstrate all originate in the characteristic non-exponential form of relaxation processes in viscous liquids and glasses. That the NMR data can only be properly interpreted by introducing appropriate non-exponential relaxation functions has already been shown by Ngai and colleagues<sup>(8)</sup> and subsequently, Muller-Warmuth and co-workers.<sup>(9)</sup> Ngai,<sup>(8,10)</sup> in particular, has shown that the stretched exponential relaxation function which accounts for the conductivity data in certain systems also accounts for the deviation from BPP behavior in NMR relaxation time temperature dependences.

The principal data used in this presentation have been reported in different form in a previous publication where they were used to compare the characteristic relaxation times for conductivity with those for mechanical relaxation in the same glass.<sup>(11)</sup> The system was chosen for its exceptionally high conductivity at  $T_g$ , implying a very high decoupling of the conductivity modes from the viscous modes. Data of high quality for a second, but less decoupled, glass are available for the case of lithium phosphate glasses, also from previous work,<sup>(12)</sup> and will be utilized to demonstrate the generality of the phenomena under discussion.

## EXPERIMENTAL

Silver iodoborate glasses were obtained by fusion of weighed quantities of analytical grade predried chemicals,  $\text{AgNO}_3$ ,  $\text{AgI}$  and  $\text{B}_2\text{O}_3$ , followed by fusion at 950K for 20 min. Care was taken to minimize the oxidation of iodide to iodine which occurs rather rapidly in exposed samples at high temperatures. After quenching to 2 mm thick discs between metal plates, the glasses were immediately transferred to a Hummer sputtering unit, and gold electrodes in the form of a three electrode configuration were sputtered onto the discs. Samples were then mounted in a hermetically sealed stainless steel cell in which electrode contact was maintained by spring pressure, and measurements were conducted in the frequency range 12-10<sup>5</sup> Hz using an automated GenRad Digibridge Model 1689 in a manner described earlier.<sup>(12)</sup> Equivalent samples were studied in the superconducting 5.169T magnetic field of a homebuilt NMR. <sup>109</sup>Ag resonates at 10.236 MHz in this field. The variation of  $T_1$  with temperature was recorded between the limits 140 and 600K.<sup>(13)</sup>

The preparation and conductivity measurement procedure for the lithium phosphate glass has been described in detail previously.<sup>(9)</sup>

## RESULTS

The frequency dependence of the conductivity for the silver glass is presented in Fig. 1. It can be seen that at the highest temperatures studied, which are still some 400K below the glass transition temperature, the onset of a frequency dependent conductivity over and above the weak variation characteristic of the "plateau" values in this system, only occurs at the high end of the available frequency range. The decrease at the low frequency extreme is due to onset of an electrode polarization phenomenon and this has a timescale which is much longer than that for the bulk sample and normally does not interfere. However, its time scale is also temperature-dependent and hence moves into our frequency window at the highest temperatures. At the lowest temperatures explored, 116K, the DC conductivity plateau has moved out of range to

lower frequencies and a considerable range of data in which the conductivity is directly proportional to frequency is exposed. This regime and its extrapolation to merge with far infrared absorption data are described in previous papers dealing with related systems<sup>(14,15)</sup> and will not be repeated here.

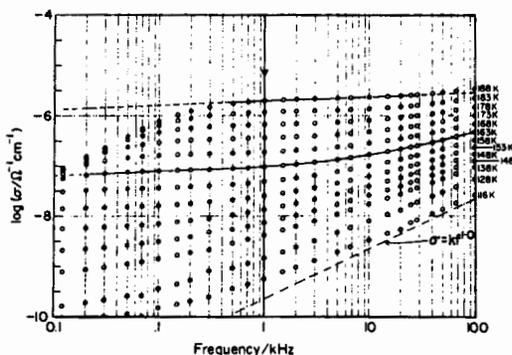


Figure 1. Electrical conductivity as a function of applied field frequency for 60 AgI-40(Ag<sub>2</sub>O·2B<sub>2</sub>O<sub>3</sub>) glass. At 1 KHz data at T < 163K are in the frequency-dependent regime.

A plot equivalent to Fig. 1 for a Li<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> glass has been shown previously<sup>(12)</sup> and will be seen later in the Discussion section. It has wide regions of true frequency-independent conductivity which suggests in this case that effects caused by poor electrode surfaces and contacts have been minimized. Selections from these data have been reproduced on the left-hand side of Fig. 6 and will be described in detail below. NMR results have been presented elsewhere<sup>(13)</sup> but the essential results for a composition close to that of Fig. 1 is reproduced in Fig. 2a, showing the minimum in  $(T_1)^{-1}$  at which temperature the condition  $\omega\tau \sim 1$  is satisfied. Fig. 2b shows the equivalent plot for a Li<sub>2</sub>O + P<sub>2</sub>O<sub>5</sub> glass taken from Ref. 9.

## DISCUSSION

To obtain data in a form suitable for comparison with data from NMR studies, we must select certain fixed frequencies from the range studied in Fig. 1 and present the data as a function of temperature for these frequencies. This is done in Fig. 3 for four frequencies between 12Hz and 10<sup>5</sup> Hz. Note the departures from the d.c. conductivity-temperature function, which occur at higher temperatures the higher the frequency held constant. The a.c. conductivity has a lower *apparent* activation energy but this is not a meaningful quantity as we discuss later. That it should be regarded with suspicion is suggested by the very low (and apparently frequency-dependent) values of the pre-exponents.

Since data extracted from the NMR studies are usually in the form of relaxation times, it is also appropriate to plot the conductivity data as conductivity relaxation times. These are obtained by using the conductivity and capacitance data obtained in the bridge measurements to construct real  $M'$  and imaginary  $M''$  parts of the complex electrical modulus<sup>(1)</sup> and taking the conductivity time as the  $1/2\pi f_{\max}$ , where  $f_{\max}$  is the frequency at the  $M''$  (loss) maximum.  $M'$  and  $M''$ , presented previously elsewhere<sup>(8,11)</sup> are reproduced in Fig. 4. The relaxation times

extracted from the Fig. 4 plots prove to have a temperature dependence identical to that of the d.c. conductivity so may be presented on the same graph using simply an extra Y axis scale. Average (as opposed to most probable) relaxation times may also be obtained from the d.c. conductivity measured at higher temperatures, using the relation<sup>(1)</sup>

$$\langle \tau_{\sigma} \rangle = \epsilon_0 / M_{\infty} \sigma_{dc} \quad (1)$$

where  $\epsilon_0$  is the permittivity of free space and  $M_{\infty}$  is the high frequency modulus defined in Fig. 3. It should be noted here that the relaxation times obtained in the above manner will *always* have the temperature dependence of the d.c. conductivity if  $M_{\infty}$  is independent of temperature, as in Fig. 4.

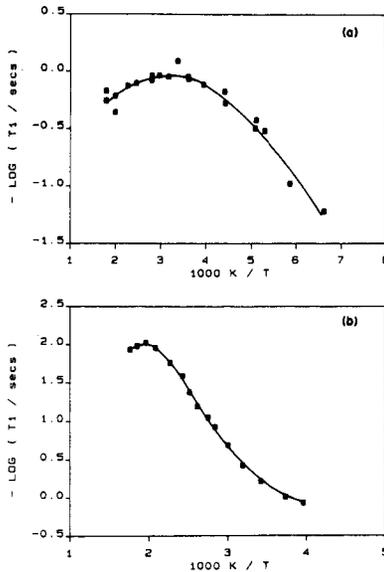


Figure 2. Logarithm of the inverse spin-lattice relaxation times for  $^{107}\text{Ag}$  in  $0.65 \text{ AgI} \cdot 0.35(\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3)$  (part a) and for  $^7\text{Li}$  in  $60 \text{ Li}_2\text{O} \cdot 40\text{P}_2\text{O}_5$  (part b), as function of reciprocal temperature. Note the much broader temperature range over which the  $^{107}\text{Ag}$  data extends, and also the greater range above the  $1/T_1$  maximum made possible by the greater conductivity mode decoupling in this case.

Following Ref. (1), the onset of a frequency dependence in the conductivity would *not* be observed if the electrical relaxation were exponential in nature. In that case, extraction of meaningful relaxation times from conductivity data would *not* depend on choosing data of sufficiently low frequency to avoid the frequency-dependent effect. A plot of  $M''$  vs.  $f$ , such as those of Fig. 4, would be a Lorentzian and knowing any point on the curve (e.g. from a single frequency measurement) would permit accurate determination of the relaxation time (and the temperature dependence of this relaxation time would automatically be identical with that of the d.c. conductivity). On the other hand, if the departure from exponential relaxation is overlooked, and the relaxation time obtained is calculated from a fixed frequency point on the high frequency side of the loss

curve,  $M''$  in Fig. 3, assuming it is Lorentzian, then that relaxation time will be an underestimate. In this case, a set of relaxation times calculated at a fixed frequency e.g. 1 KHz from data obtained at different temperatures will then give a different (and lower) temperature dependence for  $\tau_\sigma$  values obtained at low T when the loss peak maximum is below the measuring frequency. Such a data set would, in fact look like the plot of the fixed frequency a.c. conductivity data seen in Fig. 3.

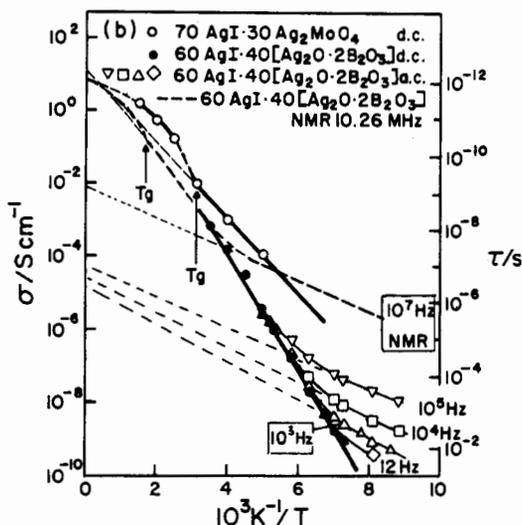


Figure 3. d.c. and a.c. conductivity (left hand scale), and conductivity relaxation and interpolated NMR correlation times (right hand scale) for 60AgI-40(Ag<sub>2</sub>O-2B<sub>2</sub>O<sub>3</sub>) glass. Behavior of d.c. conductivity in the liquid state showing onset of increased temperature dependence at  $T_g$  is illustrated by data for 70AgI-30Ag<sub>2</sub>MoO<sub>4</sub> system (Ref. 16). Note: breaks in temperature dependence of conductivity when measuring frequency (marked on plots) exceeds  $1/2\pi\tau_\sigma$ , where  $\tau_\sigma$  is conductivity relaxation time. NMR correlation times are calculated from  $T_1$  data assuming exponential relaxation.

We are now in a position to introduce the data calculated from  $1/T_1$  data for the same glass. Data similar to those shown in Fig. 2a were obtained for three compositions in the system AgI-Ag<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> over a range of temperatures by Martin et. al.<sup>(13)</sup>, and it is simple to interpolate a plot of the correlation times for the fluctuating magnetic fields causing the <sup>107</sup>Ag relaxation in a glass of the same composition for which we report the conductivity data in Figs. 1 and 3. The interpolated data are shown in Fig. 3 as a dashed line marked "10<sup>7</sup>Hz NMR" to emphasize the important point that the NMR measurements are carried out at fixed frequencies which are higher than those generally used in conductivity studies. Such frequencies will therefore be greater than the inverse relaxation time for ionic migration in all except the best (most decoupled) fast ion conductors studied at the highest temperatures. Even for the very favorable iodoborate case the  $\tau$  data reported in Ref. 13 for compositions near ours are mostly obtained at temperatures below the minimum in  $(T_1)^{-1}$  and exhibit an activation energy considerably below that of the d.c. conductivity.

The low activation energy for NMR relaxation relative to the d.c. conductivity value is comparable to the values exhibited by the a.c. conductivity. In view of our discussion on the behavior of the conductivity relaxation times which would be obtained under the assumption of exponential relaxation, this is almost certainly to be interpreted in the same terms. The same observations may be made for the results obtained on the less conducting system  $60\text{Li}_2\text{O}\cdot 40\text{P}_2\text{O}_5$  presented in Fig. 5. In this case the frequency-independent regime (above the  $1/T_1$  maximum) is

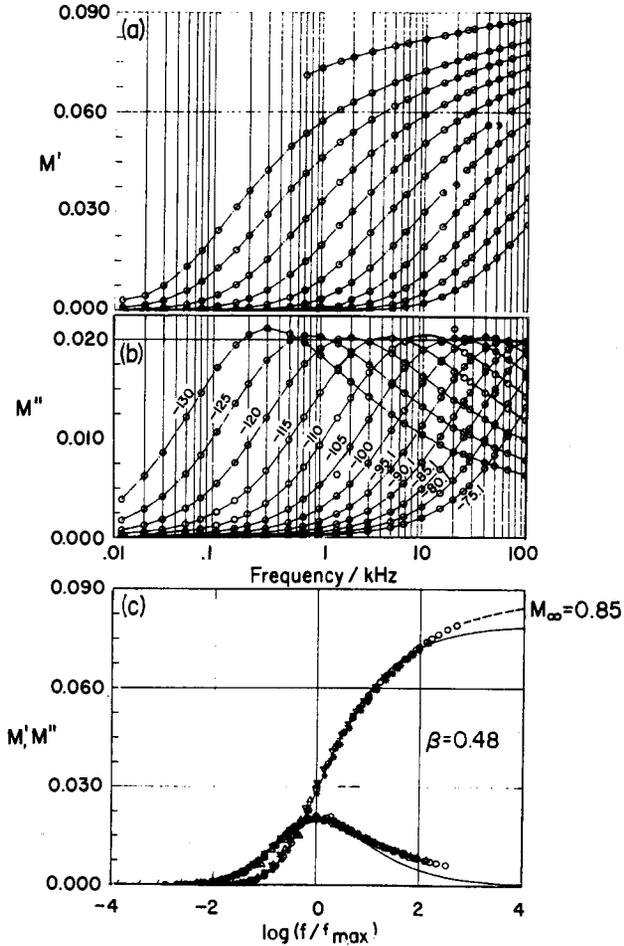


Figure 4. (a) Real  $M'$ , (b) imaginary  $M''$  parts of electrical modulus for  $60\text{AgI}\cdot 40(\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3)$  at various temperatures, (c) Master plots for  $M'$  and  $M''$  obtained by shifts along frequency axis to superimpose peak maxima. Lines through most points are from  $\theta(t) = \exp(-[t/\tau]^\beta)$

even more inaccessible, but a.c. "activation energies" closer to the d.c. values will be obtained because the departure from exponential relaxation is less extreme for the poorer conductors.<sup>(12)</sup>

Let us now consider, in the light of the extensive a.c. conductivity data, whether there is any significance to the "activation energy" obtained from the constant frequency data in the a.c. regime. The lower activation energies have, after all, previously often been discussed in terms of smaller barriers for local processes probed by the NMR measurement.

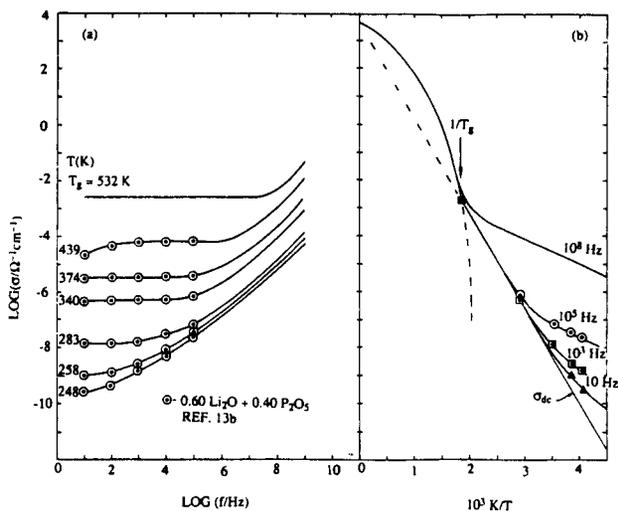


Figure 5. a.c. conductivity of 60 Li<sub>2</sub>O-40P<sub>2</sub>O<sub>5</sub> as function of frequency (part a) and reciprocal temperature showing frequency-dependent "activation energy" in the a.c. regime, and expected behavior at NMR frequency 10<sup>8</sup> Hz.

The answer to this question is contained in the master plot for the  $M'$  and  $M''$  data seen in Fig. 3. This plot shows that the relaxation spectra from all temperatures can be collapsed onto a single curve. Such superposability tells us that, while the relaxation process cannot be characterized by a single time constant, all elements of the relaxation spectrum have the same activation energy. If short time elements of the process in fact resulted from processes of smaller energy barrier, then the temperature-dependence of higher frequency elements would be smaller and the spectrum would have to "narrow up" at higher temperatures. While this may, in fact, happen at sufficiently high temperatures, (and frequencies<sup>(11)</sup>) it certainly does not happen in the range of the Fig. 1 data. Therefore the low a.c. conductivity "activation energy" *cannot* correctly be viewed as reflecting a low activation energy process. If an interpretation of the a.c. region is to be given at all it must be in terms of the value of the non-exponentiality parameter ( $\beta$  in the useful "stretched exponential" relaxation function<sup>(10,12)</sup>) for which a generally accepted explanation is still lacking.

As far as the temperature range *above* the  $1/T_1$  maximum is concerned the Arrhenius plot of  $1/T_1$  against  $1/T$  will certainly be characterized by a higher activation energy since the non-

exponential relaxation function of the stretched exponential type distorts the high frequency side of the spectrum (corresponding to the low  $1/T$  side of the Arrhenius plot for constant frequency measurements) more than the low frequency (high  $1/T$ ) side. Thus the relaxation times assessed using BPP theory will be closer to the correct values, and the activation energy therefore close to that for d.c. conductivity. However, for highly non-exponential processes such as for the silver iodoborate glass, discrepancies are still to be expected, and are found<sup>(13)</sup>.

The noise level for  $^{127}\text{Ag}$  NMR studies is unfortunately too high to permit accurate empirical resolution of these questions. We hope to obtain a clearer empirical base by study of systems with comparable decoupling indexes but more favorable NMR nuclei. Lithium chloroborate glasses, for instance, have such a high decoupling of conductivity from viscous modes that a Brillouin linewidth maximum (analogous to the  $1/T_1$  maximum) has been observed below  $T_g$ .<sup>(37)</sup> Since the frequency held (approximately) constant in the Brillouin scattering experiment is  $\sim 28$  GHz, far above the NMR frequency, and since  $^7\text{Li}$  is an excellent NMR nucleus, this would appear to be a most promising system. It is currently under study at multiple field frequencies and results, including comparisons of NMR with a.c. conductivity, will be published in subsequent articles.<sup>(18,19)</sup> A more general and extended discussion of the principal points of this paper can be found in Refs. 5 and 7.

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