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# Fast ionic conduction in Na<sub>2</sub>S+B<sub>2</sub>S<sub>3</sub> glasses: Compositional contributions to nonexponentiality in conductivity relaxation in the extreme low-alkali- metal limit

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# Fast ionic conduction in Na<sub>2</sub>S+B<sub>2</sub>S<sub>3</sub> glasses: Compositional contributions to nonexponentiality in conductivity relaxation in the extreme low-alkali-metal limit

## Abstract

The conductivity relaxation phenomenon in glassy and crystalline ionic conductors has been known for many years to be a highly nonexponential process. The stretched exponential function  $\exp(-(t/\tau)^\beta)$  has been used with varying levels of success to describe this relaxation. Whether the nonexponentiality is due to parallel conducting processes acting independently of each other and having a distribution of relaxation times or to serial processes strongly coupling the ionically conducting species and constraining each other's relaxation, the exact nature of this process is still unknown. If coupling is the active mechanism responsible for the nonexponentiality, then there should be a relationship between the extent of the nonexponentiality and the average ion separation distance; the greater the ion-ion separation, the smaller the coupling between the ions. To test this hypothesis, wide composition, frequency, and temperature range conductivity measurements have been performed on the fast-ion-conducting glass series, Na<sub>2</sub>S+B<sub>2</sub>S<sub>3</sub>. For  $x(\text{Na}_2\text{S})=0.001$ , the relaxation is nearly exponential. As the Na<sub>2</sub>S concentration increases, the estimated ion-ion separation distance decreases; so do both the dc conductivity activation energy and the  $\beta$  parameter in the stretched exponential. The  $\beta$  parameter, however, shows a much stronger dependence to the ion-ion separation distance. It is also found that for nearly all of the glasses studied to date, the composition dependencies of the  $\beta$  parameter can be cast onto a master plot of  $\beta$  versus average ion-ion separation distance. In this way, we provide a universal trend for the compositional dependence of the nonexponentiality in glass.

## Disciplines

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## Comments

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## Fast ionic conduction in $\text{Na}_2\text{S} + \text{B}_2\text{S}_3$ glasses: Compositional contributions to nonexponentiality in conductivity relaxation in the extreme low-alkali-metal limit

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The conductivity relaxation phenomenon in glassy and crystalline ionic conductors has been known for many years to be a highly nonexponential process. The stretched exponential function  $\exp-(t/\tau)^\beta$  has been used with varying levels of success to describe this relaxation. Whether the nonexponentiality is due to parallel conducting processes acting independently of each other and having a distribution of relaxation times or to serial processes strongly coupling the ionically conducting species and constraining each other's relaxation, the exact nature of this process is still unknown. If coupling is the active mechanism responsible for the nonexponentiality, then there should be a relationship between the extent of the nonexponentiality and the average ion separation distance; the greater the ion-ion separation, the smaller the coupling between the ions. To test this hypothesis, wide composition, frequency, and temperature range conductivity measurements have been performed on the fast-ion-conducting glass series,  $\text{Na}_2\text{S} + \text{B}_2\text{S}_3$ . For  $x(\text{Na}_2\text{S})=0.001$ , the relaxation is nearly exponential. As the  $\text{Na}_2\text{S}$  concentration increases, the estimated ion-ion separation distance decreases; so do both the dc conductivity activation energy and the  $\beta$  parameter in the stretched exponential. The  $\beta$  parameter, however, shows a much stronger dependence to the ion-ion separation distance. It is also found that for nearly all of the glasses studied to date, the composition dependencies of the  $\beta$  parameter can be cast onto a master plot of  $\beta$  versus average ion-ion separation distance. In this way, we provide a universal trend for the compositional dependence of the nonexponentiality in glass.

### I. INTRODUCTION

The impedance spectrum of glassy ionic conductors is completely characterized once the dc conductivity preexponent ( $\sigma_0$ ), dc activation energy ( $E_{\text{act}}$ ), the high-frequency dielectric constant ( $\epsilon_\infty$ ), and the fractional (Kohlrausch) exponent  $\beta$  used to describe the nature of the frequency dispersion of the conductivity, are known. The conductivity dispersion was related to the nonexponential conductivity relaxation in the time domain by Macedo, Moynihan, and Bose.<sup>1</sup> Following the usage by Williams and co-workers<sup>2-4</sup> of the Kohlrausch decay function,

$$\Phi(t) = \exp-(t/\tau)^\beta, \quad 0 < \beta < 1. \quad (1)$$

Moynihan, Boesch, and Laberge<sup>5</sup> recognized that the Fourier transform of the derivative of the decay function could give an excellent description of the conductivity dispersion in ion-conducting glasses. This result has since been documented for these and many other systems, especially by Ngai and others.<sup>6-9</sup>

Martin and Angell,<sup>8,10</sup> Ngai and Martin,<sup>11</sup> Mundy and Jin,<sup>12-14</sup> and Ngai and co-workers<sup>7,11</sup> have reported for various glasses the compositional contributions to the nonexponential conductivity relaxation.  $\beta$  values for all these glass systems are far less than one and are weakly compositional dependent. However, Ngai *et al.*<sup>7</sup> report from their work on alkali-metal germanates and aluminogermanates and Simmons *et al.*<sup>15</sup> report from their work on alkali-metal silicates, that exponential relaxation ( $\beta=1$ ) may be achieved by reducing the cation

concentration to below 1%. Ngai<sup>6</sup> in his coupling model uses the anticorrelation parameter,  $n \equiv 1 - \beta$ , to show the extent to which cations interact (couple) during conducting and, therefore, the extent of nonexponentiality. He explains the approach to single relaxation ( $\beta=1$ ) may be associated with a decrease in cation-cation interactions characterized essentially by independent cation jumps relaxing in analogy to Debye dipoles.

Martin<sup>10</sup> tested the above hypothesis by calculating the average cation-cation separation distances ( $\alpha$ ) from the density and composition for various sodium-modified oxide glasses and plotting  $\alpha$  against the  $\text{Na}_2\text{O}$  mole fraction, see Fig. 1(a). This figure shows that  $\alpha$  exhibits its greatest composition dependence for  $x < 0.2$  and thereafter  $\alpha$  decreases slowly with composition. Furthermore, Martin created a master plot of  $\beta$  against the cation-cation separation distance for a whole series of glasses and this is reproduced in Fig. 1(b). The data show that for  $\alpha$  less than 10 Å, all glasses exhibit  $\beta$  values  $\approx 0.5$ , while for large  $\alpha$  (extremely alkali-metal dilute glass),  $\beta$  increases to unity implying a drastic decrease in cation-cation coupling. The compositional variation of  $\beta$  between the two extremes remains an open question. The intent of this study is to bridge the gap between the extremely low-alkali-metal exponential region and the high-alkali-metal nonexponential region.

Impedance spectroscopy techniques have not typically been used to probe the conductivities of glasses modified by very low concentration of alkali-metal ions because of instrument limitations in measuring extremely low conductivities [ $10^{-10}$  ( $\Omega \text{ cm}$ )<sup>-1</sup>]. Much ionic conductivity data, therefore, have been gathered for glasses in the

range of 2–80 mol % alkali-metal content,<sup>8,10,16–18</sup> but very few for glasses with alkali-metal contents less than 1 mol %.<sup>7,15,19</sup> The low-composition limit, as suggested by Martin,<sup>10</sup> however, may be overcome by investigating glasses with extremely high  $T_g$ 's, whereby increasing the temperature may increase the conductivity to a measurable range, or alternatively, by studying glasses where the mobility per cation is so high that the conductivity remains measurable even for very low carrier content, such as the case for chalcogenide glasses.<sup>20–26</sup>

An ideal glass system to investigate the nonexponentiality question in the low-alkali-metal limit should not only have a high ionic conductivity, but also a low-alkali-metal forming region. One example of such a system is the chalcogenide series  $x(\text{Na}_2\text{S}) + (1-x)\text{B}_2\text{S}_3$ , for which Levasseur *et al.*<sup>25</sup> and Ravine and Souquet<sup>26</sup> have reported room-temperature conductivities for  $0.29 < x(\text{Na}_2\text{S}) < 0.41$  of greater than  $10^{-6} (\Omega \text{cm})^{-1}$  and Martin and Bloyer<sup>27,28</sup> have shown through their infrared

studies of these glasses that there exists a homogeneous glass-forming region for  $0 \leq x(\text{Na}_2\text{S}) \leq 0.25$ . Using this glass system then, we present a complete examination of the effects of glass composition on the exponent  $\beta$  in the stretched exponential function. We specifically seek to address the hypothesis that  $\beta$  can best be correlated with the cation separation distance,  $\alpha$ .

## II. PREPARATION OF $x(\text{Na}_2\text{S}) + (1-x)\text{B}_2\text{S}_3$ GLASSES

High-purity  $\nu\text{-B}_2\text{S}_3$  was prepared using the method described by Boyer and Martin.<sup>27</sup> Appropriate amounts ( $\pm 0.001$  g) of boron (amorphous,  $< 1 \mu\text{m}$ , 99.9% pure, Cerac) and sulfur (6N, Cerac) were weighed for stoichiometric  $\text{B}_2\text{S}_3$  and then sealed in an evacuated carburized silica tube. The tube was then heated in a rotating tube furnace at a heating rate of  $2^\circ\text{C}/\text{min}$ . from room temperature to  $-850^\circ\text{C}$  and then held at that temperature for 8 h. The glassy product cooled to room temperature and then was removed from the tube, finely ground, resealed in another carburized tube and reheated to  $850^\circ\text{C}$ , as before, to insure homogeneous  $\nu\text{-B}_2\text{S}_3$ . All operations except heating were performed in an  $\text{O}_2$  and  $\text{H}_2\text{O}$ -free glovebox.

$x(\text{Na}_2\text{S}) + (1-x)\text{B}_2\text{S}_3$  glasses in the range  $0.05 < x$ , were also prepared in an  $\text{O}_2$  and  $\text{H}_2\text{O}$ -free glovebox. 2.5 g batches of  $\text{Na}_2\text{S}$  (99.9% pure, Cerac) and  $\text{B}_2\text{S}_3$  were carefully weighed out ( $\pm 0.001$  g). The mixture was then melted in a covered vitreous carbon crucible at  $-800^\circ\text{C}$  in a Mo-wire wound furnace for 5–10 min.

The preparation of glasses using the above technique for compositions  $x < 0.05$  showed weight losses of the same order of magnitude as the quantity of  $\text{Na}_2\text{S}$  used to prepare the 2.5 g samples. To overcome this problem, glasses were prepared by diluting a measured amount of  $x = 0.05$  glass in pure  $\text{B}_2\text{S}_3$  to make compositions in the range of  $0.01 < x < 0.05$ . Further dilution of  $x = 0.01$  glass with pure  $\text{B}_2\text{S}_3$  was used to prepare glasses of even lower sodium compositions.

All melts were quenched from 800 to  $280^\circ\text{C}$  in stainless-steel mold and given an identical thermal history. Samples were sputtered with gold electrodes and ionic conductivity measurements were performed over the frequency range of 1 Hz–1 MHz and over the temperature range of 300–500 K by using a computer controlled Solarton 1250 analyzer and a homebuilt conductivity cell.<sup>29</sup>

## III. RESULTS AND DISCUSSION

### A. dc conductivity

The predominant interest in investigating fast-ion-conducting (FIC) glasses has been to optimize the dc conductivity for their use as solid electrolytes in solid-state batteries. Figure 2 shows the Arrhenius plot of the dc conductivity. As seen in all other studies of FIC glasses, the dc ionic conductivity increases with an increase in temperature and an increase in sodium content.

The dc activation energy are plotted versus the log of

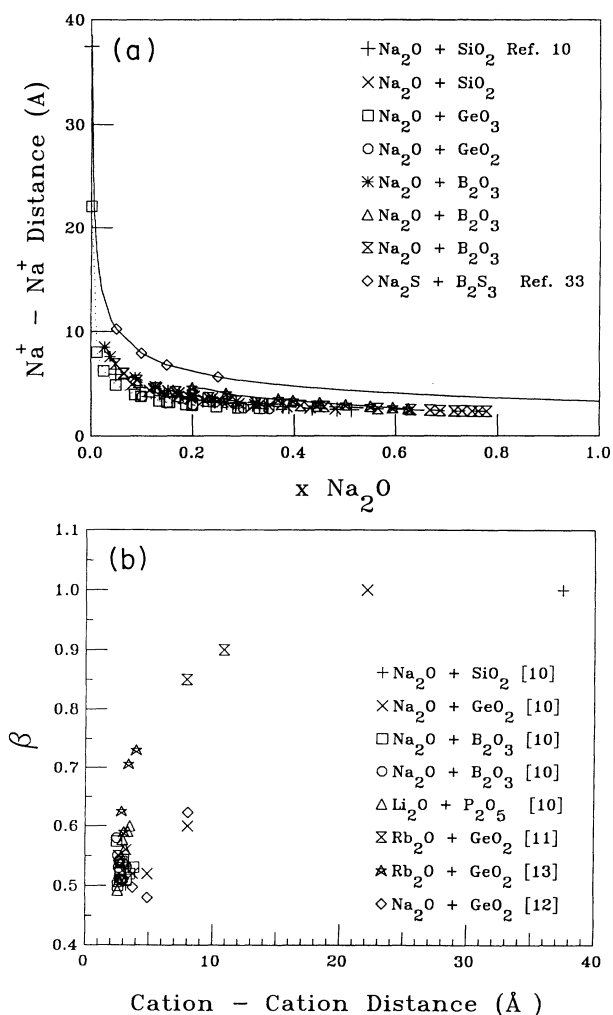


FIG. 1. (a) A plot showing the variation in the alkali-metal-alkali-metal separation distance with composition. (b) Master plot of  $\beta$  parameter plotted against cation-cation distances, reproduced from Fig. 7 in Ref. 10.

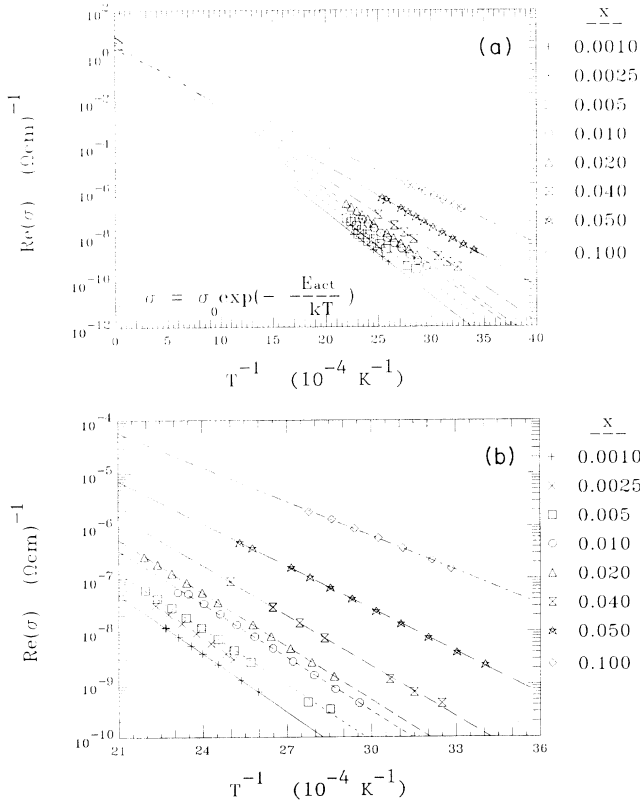


FIG. 2. Arrhenius plot of the dc conductivities obtained from the complex impedance plots of  $x(\text{Na}_2\text{S})+(1-x)\text{B}_2\text{S}_3$  composition glasses.

the composition in Fig. 3 and listed on Table I. The data on the same glasses reported by Levasseur *et al.*<sup>25</sup> are in good agreement with our results. The activation energy decreases from the asymptotic 0.75 eV value (limit as  $x \rightarrow 0$ ) to 0.35 eV at  $x=0.40$ . This result will be discussed further below.

### B. Conductivity relaxation

Isothermal frequency plots of the real part of the conductivity for the  $x=0.005$  composition glass are shown in Fig. 4(a). The data show a frequency-independent con-

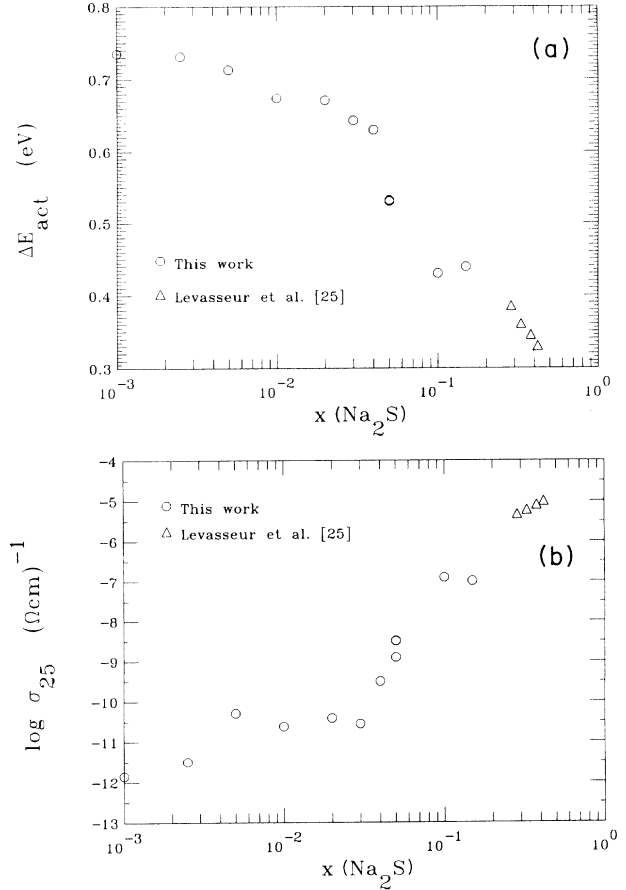


FIG. 3.  $x(\text{Na}_2\text{S})$  compositional dependency of the dc activation energy.

ductivity for low frequencies and high temperature followed by an increase in conductivity for higher frequencies and lower temperatures. The switch from the frequency independent to the dependent region signals the onset of the conductivity relaxation phenomena. In order to relate the conductivity to the relaxation of the mobile ions, one can rely on the phenomenological nature of the electric modulus,<sup>11</sup> or on the generalized Nerst-Einstein formalism.<sup>30</sup> The electrical modulus approach to analyze the relaxation phenomena is preferred as it is easier to re-

TABLE I. Electrical properties of  $\sigma(\omega)$  for  $x(\text{Na}_2\text{S})+(1-x)\text{B}_2\text{S}_3$  glasses.

$x(\text{Na}_2\text{S})$	$\sigma_0$	$\Delta E_{\text{act}}$ (eV)	$\beta$	$\epsilon_\infty$	Na-Na (Å)
0.0010	2.9	0.735	0.930	5.62	38.59
0.0025	5.6	0.731	0.870	5.81	28.41
0.0050	46.0	0.713	0.823	5.30	22.52
0.0100	4.8	0.674	0.722	6.67	17.84
0.0200	6.9	0.671	0.650		14.09
0.0300	1.4	0.643			12.25
0.0400	1.0	0.630			11.08
0.0500	2.1	0.531	0.350	6.65	10.24
0.1000	2.0	0.430	0.460	7.26	7.92
0.1500	0.4	0.439	0.500		6.81

late to other properties, especially the dynamical mechanical modulus, and can be written as a single function of the conductivity. The reader is referred to the papers by Macedo, Moynihan, and Bose<sup>1</sup> and Moynihan, Boesch, and Laberge<sup>5</sup> for the details of the electrical modulus formalism and the application of the Kohlrausch decay function.

The real part of the conductivity  $\sigma'$  is related to the complex electrical modulus<sup>1</sup> through the following expression:

$$\sigma'(\omega) = \omega \epsilon_0 \epsilon''(\omega) = \omega \epsilon_0 \frac{M''(\omega)}{|M^*(\omega)|^2}, \quad (2)$$

where  $M'$  and  $M''$  are the real and imaginary parts of the complex electric modulus,  $M^*$ , and  $|M^*|$  is the magnitude of the modulus. The modulus is determined by the inverse of the complex permittivity  $\epsilon^*$ :

$$M^*(\omega) = \frac{1}{\epsilon^*} = \frac{\epsilon'(\omega)}{|\epsilon^*(\omega)|^2} - i \frac{\epsilon''(\omega)}{|\epsilon^*(\omega)|^2} \quad (3)$$

$$\equiv M'(\omega) + iM''(\omega) \quad (4)$$

$$= M_\infty \left[ 1 - \int_0^\infty \exp(-i\omega t) \frac{d\Phi(t)}{dt} dt \right], \quad (5)$$

where  $M_\infty = 1/\epsilon_\infty$ ,  $\epsilon_\infty$  is the limiting high-frequency real part of the permittivity, and the function  $\Phi(t)$  is a relaxation function, which in our case will be the Kohlrausch electrical relaxation function, Eq. (1). The electrical modulus plots are similar in appearance and interpretation to mechanical modulus. Any change in the spectra of the real part of the modulus  $M'$  is indicative of a change in the "stiffness" of the material under test, and the frequency region where this change occurs is emphasized by a "loss" peak in the imaginary part of the modulus. Examples of both the real stiffness, and the imaginary loss parts will be discussed below.

Using Eqs. (2) and (5), the conductivity can also be related directly to the relaxation function  $\Phi(t)$ . Macedo, Moynihan, and Bose<sup>1</sup> have already shown that for a nonexponential relaxation the conductivity will exhibit a strong frequency dependence. To examine this, Fig. 4(b) shows a master plot of a series of ac conductivity curves for the glass with  $x = 0.005$ , where the frequency has been normalized by the peak frequency for that temperature of the imaginary part of the electrical modulus and the conductivity scale has been reduced by the dc conductivity  $\sigma_{dc}$ . As expected, the curves are superimposable in accordance with the temperature independence of the relaxation function and the superposition principle. Figure 5 shows a similar plot but not of a series of glasses. Here all the temperatures were chosen such that each glass would have approximately the same relaxation frequency  $\sim 1$  kHz. In this way, each curve would have about the same data region above and below the peak frequency in the imaginary modulus. Figure 5 shows that as alkali-metal is added to the glass, the frequency depen-

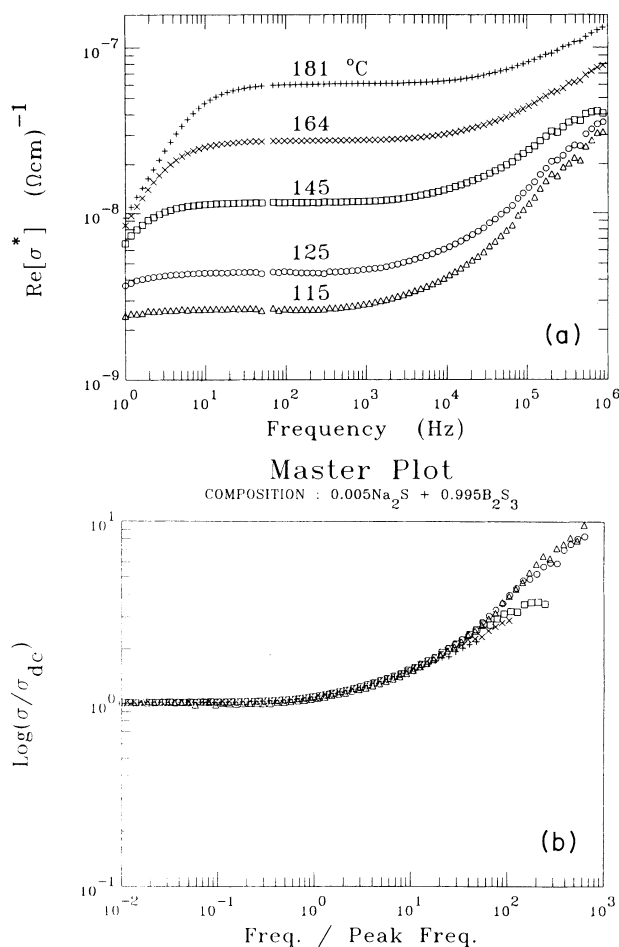


FIG. 4. (a) Plot of the isothermal frequency-dependent conductivity for a series of temperatures for  $0.005\text{Na}_2\text{S} + 0.995\text{B}_2\text{S}_3$  glass. (b) Master plot of the normalized  $\sigma_{dc}$  conductivity plotted against a normalized frequency. Peak freq. is the frequency of the corresponding peak in the electrical modulus curves at the same temperature.

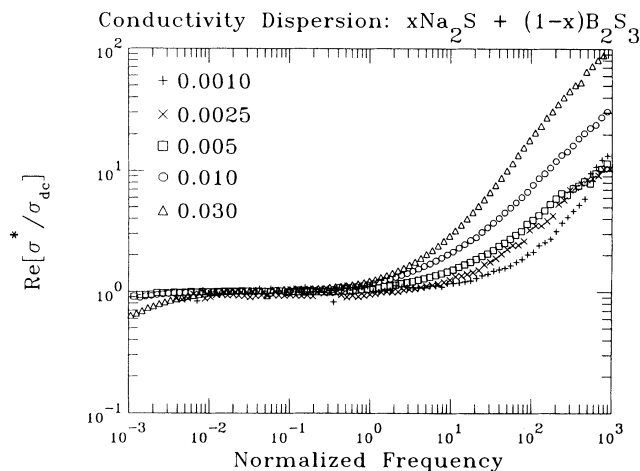


FIG. 5. Conductivity for a series of  $x(\text{Na}_2\text{S}) + (1-x)\text{B}_2\text{S}_3$  glasses.

dence of the conductivity increases. Note that for low-alkali-metal glasses, there is a range of frequencies above  $f/f_0 \approx 1$  where the conductivity remains frequency independent. It is not clear at this point whether the increase in conductivity at the lowest  $x$  and highest frequency arises from conductivity relaxation or from another loss mechanism. We are investigating this question through the use of conductivity measurements up to 1 GHz.<sup>31</sup>

Figure 6 shows a series of isothermal frequency spectra

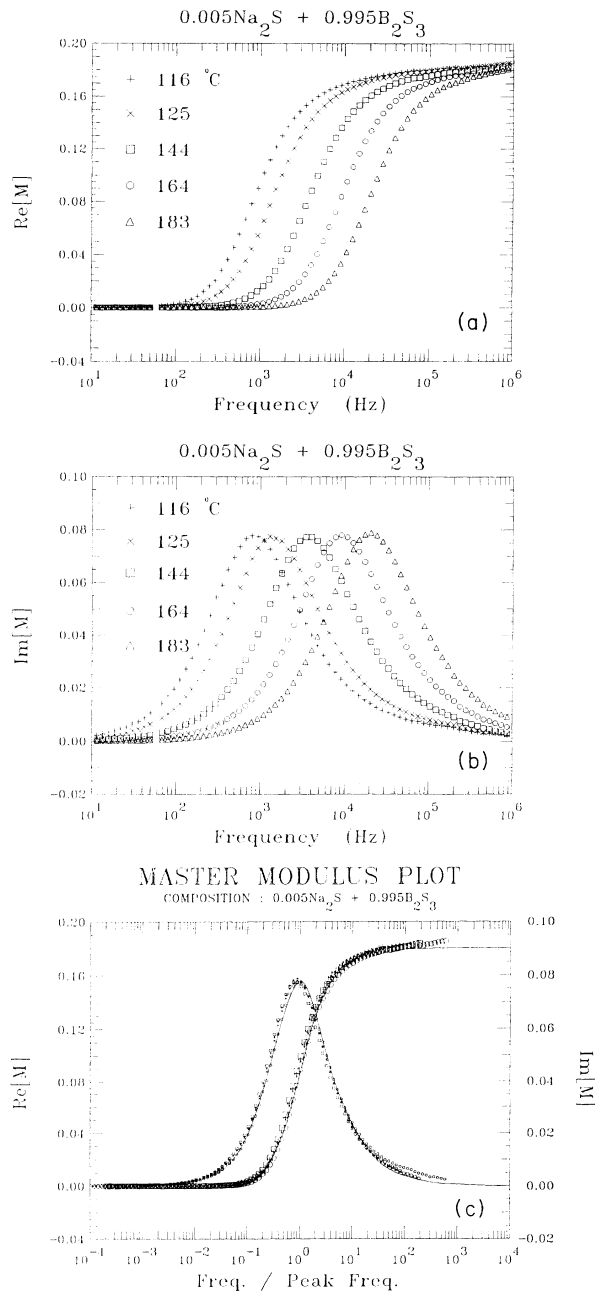


FIG. 6. Plots of the isothermal frequency spectra of (a)  $M'$ , (b)  $M''$ , and (c) the superimposed  $M'$  and  $M''$  for a series of temperatures for 0.005Na<sub>2</sub>S+0.995B<sub>2</sub>S<sub>3</sub> glass. Line through the data is the best fit of Eq. (5) with  $\beta=0.82$ .

of (a)  $M'$ , (b)  $M''$  and (c) the superimposed  $M'$  and  $M''$  for  $x=0.005$  composition glass. The low-frequency value of  $M'$  is zero and represents a lack of restoring force for the electric-field-induced mobile sodium ions. This is analogous to mechanical modulus for viscous flow where there is a lack of restoring force at low frequencies under the influence of a steady shear force. As frequency increases,  $M'$  increases to a maximum asymptotic value defined as  $M_\infty$ . If it is envisioned that as frequency increases, each ion moves a shorter and shorter frequency electric field until finally, the electric field changes so rapidly that the ions only “rattle” within the confinement of their potential energy wells.<sup>8</sup> At these frequencies, the glass appears to have become “stiffer” because the mobile ions have been frozen into the structure of glass.

The spectra of  $M''$  shows an asymmetric peak approximately centered in the dispersion region of  $M'$ . The region to the left of the peak is where the ions are mobile over long distances, and the region to the right is where the ions are spatially confined to their potential wells. The region where the peak occurs is indicative of the transition from long-range to short-range mobility or more quantitatively defined as the condition where  $\omega\tau_\sigma \approx 1$ , where  $\tau_\sigma$  is defined as the most probable ion relaxation time.

The superimposed plots in Fig. 6(c) were obtained by scaling each frequency by the frequency of the maximum loss in  $M''$ .<sup>8</sup> The near perfect overlap of the different temperature data, superimposed on the single master curve, illustrates well that all dynamic processes occurring at different frequencies exhibit the same thermal activation energy. This result was also observed in Fig. 4(b) for the conductivity. The temperature dependence of the peak relaxation frequency for the glass with  $x=0.005$  is shown in Fig. 7. The dc activation energy and the  $M''$  peak frequency activation energy (from Fig. 7) agree quite well. As described in a previous paper,<sup>10</sup> the temperature independence of the loss peaks contradicts the

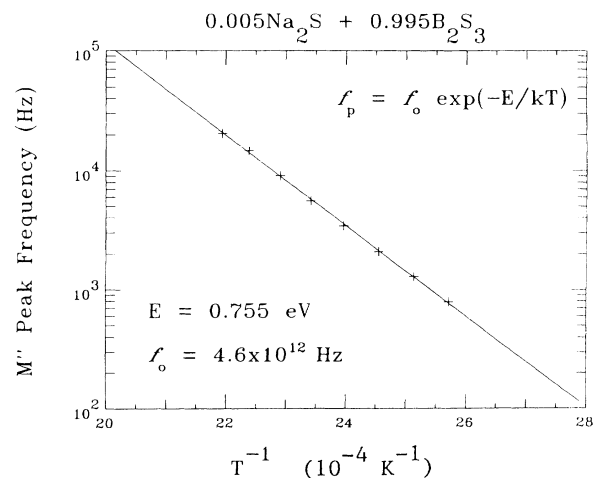


FIG. 7. Arrhenius plots of the frequency at the maximum value of the imaginary part of modulus for 0.005Na<sub>2</sub>S+0.995B<sub>2</sub>S<sub>3</sub> composition glasses.

idea of a distribution of activation energies that has been suggested to explain the conductivity dispersion.<sup>8-10</sup>

Plots similar to those shown in Fig. 6, obtained for other glass compositions, differ only in the maxima value and the magnitude of the full width half maximum (FWHM) for  $M''$  loss peak. The compositional dependence of the shape of the electrical modulus curves is quite apparent from the normalized frequency complex modulus plots for four different composition glasses shown in Fig. 8 where Fig. 8(a) shows the real and Fig. 8(b) shows the imaginary part of the modulus. Here as with Fig. 4(b), the temperature for each glass was chosen such that the relaxation frequency is about the same,  $\sim 1$  kHz. The dramatic narrowing with decreasing  $x$  is quite evident and suggests the strong role that composition has upon the conductivity relaxation in the low-alkali-metal region.

The shape of each spectrum for each glass composition is quantified with a  $\beta$  value obtained by fitting the  $M'$  and  $M''$  curves to the Kohlrausch relaxation function by the method of Moynihan, Boesch, and Laberge.<sup>5</sup> The initial value for  $\beta$  is determined from the magnitude of the FWHM of the  $M''$  loss peak.  $\beta$  is then graphically fine tuned by overlapping precalculated modulus curves on the experimental data. By varying the magnitude of  $M_\infty$  and  $\beta$  for the fitting curve, the disagreement between the experimental data and the fit is easily minimized. This whole process is computer automated using an im-

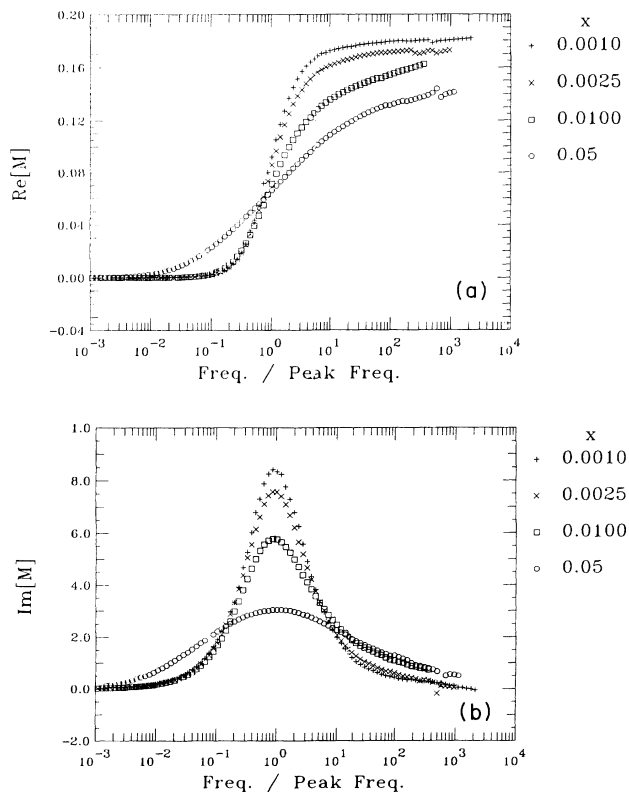


FIG. 8. (a) The real and (b) imaginary part of the electrical modulus plotted against normalized frequency for a few selected glasses in the series  $x(\text{Na}_2\text{S}) + (1-x)\text{B}_2\text{S}_3$  composition.

pedance spectroscopy analysis software package developed by one of the authors (H.P.).<sup>29</sup> The smooth line through the modulus data in Fig. 6(c) is a typical example for the various glass compositions of the close agreement between the experimental data and the curve fit. The glass in Fig. 6(c) has a  $\beta$  value of 0.83 and  $\beta$  values obtained for other composition glasses are given in Table I and plotted in Fig. 9 against composition.

The  $\beta$  parameter decreases to a minimum value of  $\sim 0.35$  for the  $x=0.05$   $\text{Na}_2\text{S}$  composition glass and then rapidly approaches 1 for  $x \leq 0.05$ . We believe this clearly shows the transition between the nonexponential and exponential relaxation phenomena in glass. This approach towards exponential relaxation with reduced alkali-metal content agrees well with the predictions of Simmons *et al.*,<sup>15</sup> Ngai,<sup>6</sup> and Martin.<sup>10</sup> The electrical modulus data with a  $\beta$  of 0.93 for the  $x=0.001$   $\text{Na}_2\text{S}$  glass in Fig. 10 shows a nearly single exponential relaxation, almost identical to the modulus response of an ideal RC circuit.

To further investigate the hypothesis that the approach to single exponential relaxation ( $\beta \rightarrow 1$ ) may be associated with the lack of cation-cation interactions,<sup>6,15</sup>  $\beta$  is plotted against the average Na-Na separation distance ( $\alpha$ ) in Fig. 11, similar to Fig. 1(b). The Na-Na separation distances were calculated using the assumption that the cations were uniformly distributed throughout the glass, from the composition and the density data of Martin and Polewik.<sup>32</sup> The results in Fig. 11 show that  $\beta$  increases almost linearly from 0.5 to 1 as the Na-Na separation distance increases from  $\sim 5$  to  $\sim 40$  Å and strongly suggests that the conductivity relaxation is inherently tied to this parameter. Two data points on this graph, the ones at  $\beta$ , approximately equal to 0.46 and 0.35 fall off the linear curve and the reason for this is unknown at this point. However, the electrical modulus curves like those shown in Fig. 8, do show enormous broadening, beyond what might be expected. This may suggest that in the high-alkali-metal range  $x \geq 0.05$ , extra contributions exist beyond the conductivity relaxation. The fact that the  $\beta$  value rises to unity only at the lowest-alkali-metal fraction suggests that a long-range force, such as the Coulombic force, is responsible for the interaction lead-

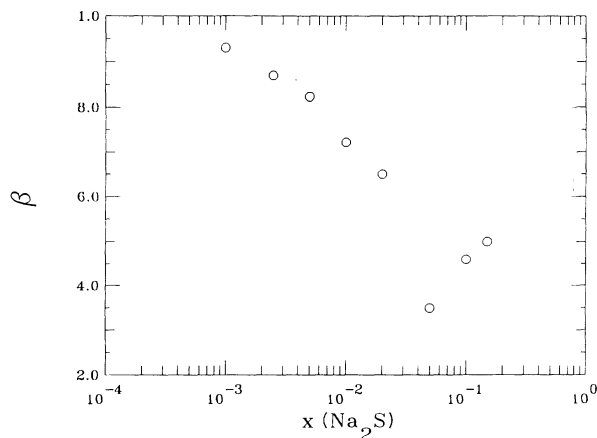


FIG. 9. Variation in the  $\beta$  parameter vs  $x(\text{Na}_2\text{S})$ .



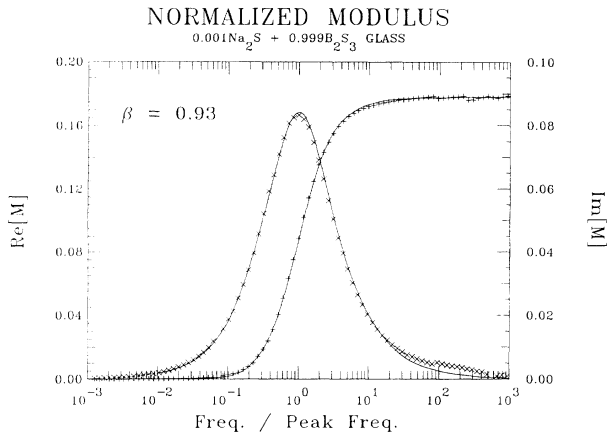


FIG. 10. Electrical modulus data for  $0.001\text{Na}_2\text{S} + 0.999\text{B}_2\text{S}_3$  glass showing near ideal single exponential relaxation. Line is best fit of Eq. (5) with  $\beta=0.93$ .

ing to nonexponentiality. Another possible mechanism might be that, as others have suggested, the mobile cations cluster, rather than disperse themselves randomly in the glass. Such an effect would cause the relaxation to retain its nonexponential character to levels of alkali-metal below that where the cations would be thought to be jumping independently of one another. At present, we cannot refute nor corroborate this possibility.

In any case the results shown in Fig. 11 and combined with those of Fig. 1(b), do show a universal behavior for all glasses examined to date. Others, especially Ngai and Martin<sup>11</sup> have correlated  $\beta$  with a "primitive" activation energy  $\beta\Delta E_{\text{act}}$ . Although this correlation does work well for many glasses, our correlation here fits  $\beta$  to a structurally recognizable variable and perhaps for this reason has more significance.

Angell<sup>9</sup> recently correlated  $\beta$  to the extent of decou-

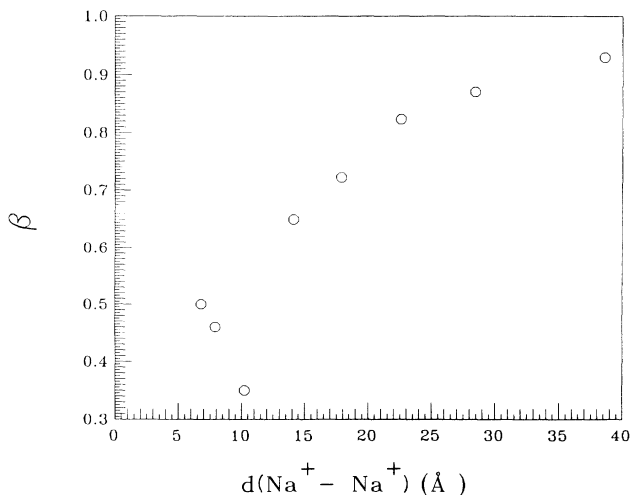


FIG. 11.  $\beta$  parameter against the average Na-Na ion separation distance  $d$ .

pling between the fast-ion diffusional motion of the mobile ion populations and the viscous liquid motions of the host glass network. Here the hypothesis is that as the ions become more and more decoupled, i.e., more mobile at constant scaled temperature (by the viscosity), they become more likely to correlate (couple to) each others motions. Ions that are highly coupled to the network of the glass are, likewise, much less likely to couple to each others motion. Using the conductivity data from Fig. 2 to calculate the decoupling index  $R_\sigma \equiv \tau_n / \tau_\sigma$  for each glass and taking  $\tau_n \sim 100$  s at  $T_g$  and  $\tau_\sigma = \epsilon_0 / M_\infty \sigma$ , Fig. 12 shows that the data for the  $\text{Na}_2\text{S} + \text{B}_2\text{S}_3$  glasses are stark exceptions to the master plot. In fact the data appear to be well correlated along a straight line but this line has a completely different slope and intercept than Angell's master plot. Other exceptions to this correlation are also known.<sup>33</sup> It is also not clear from the graph what the physical significance would be for the apparent and dramatic "bend over" at high  $\beta$  in order for the  $\text{Na}_2\text{S} + \text{B}_2\text{S}_3$  data to meet up at the proposed correlation point of  $\beta=1$  and  $R=1$ . Our data do, however, suggest that though there may well be certain classes of glasses that can be placed onto the  $\beta$  versus  $R$  universal map, there are certain exceptions to the correlation. Indeed, it may well be that such anticorrelation can be used to gain better insights into the exact nature of the nonexponential relaxation in glass.

C. Activation energy

The dependence of the activation energy on the Na-Na ion separation distance ( $\alpha$ ) is shown in Fig. 13. The plot shows a smooth connection between two regions of dependence on ion separation distance. The first region,  $\alpha < 15$  Å (for  $x > 0.02$ ), shows a strong positive dependence of the activation energy on the separation distance  $\alpha$ . The second region,  $\alpha > 15$  Å, shows a weakly dependent activation energy asymptotically approaching  $\sim 0.75$  eV.

To discuss the above observations, we proceed in the

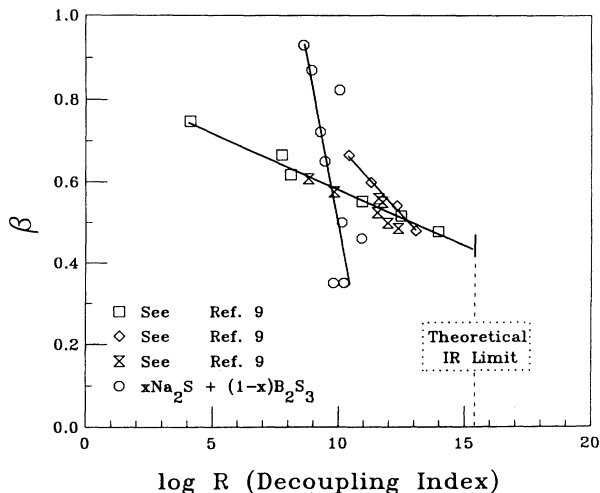


FIG. 12.  $\beta$  parameter vs the decoupling index  $R_\sigma$ .

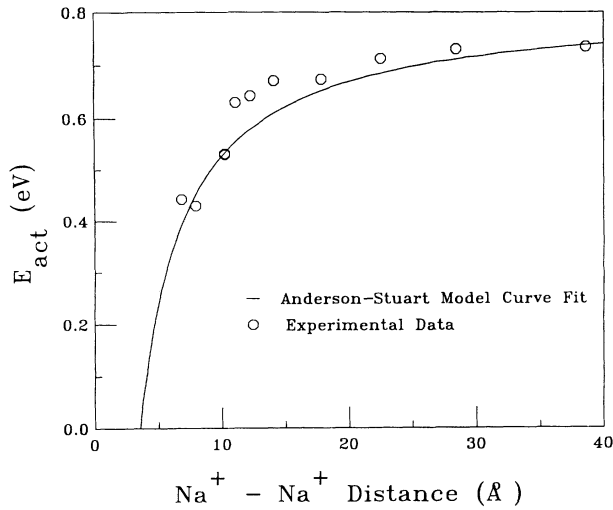


FIG. 13.  $\Delta E_{\text{act}}$  plotted against the average Na-Na ion separation distance. Line is best fit of Eq. (8).

order of decreasing alkali-metal concentration (increasing  $\alpha$ ). For the alkali-metal composition range of  $0.02 \leq x \leq 0.5$ , a strong increase in the activation energy is observed with an increase in Na-Na separation distance. This phenomenon has been widely reported for most alkali-metal glasses in a similar composition range.<sup>8,11,16,34</sup> Martin and Angell have explained this phenomenon by suggesting that the activation energy is a function of the amount of overlap between the potential energy wells of cation sites.<sup>8,34</sup> They show, through the Anderson-Stuart (AS) model,<sup>35</sup> that the energy barrier for each cation (i.e., the activation energy) increases as the overlap between potential energy wells decreases due to an increasing alkali-metal-alkali-metal ion separation distance. At high alkali-metal,  $x \geq 0.05$ , the overlap between these potential energy wells, for all practical purposes, has saturated as the ion separation distance saturates at a small value  $< 5 \text{ \AA}$ , and thereafter changes little with added alkali-metal. As the alkali-metal is decreased below  $x = 0.05$ , however, dramatic increase in  $\alpha$  occurs and as such the overlap between the potential energy wells decreases.

The trend in the activation energy observed in the very low-alkali-metal region of Fig. 13 is reported here. In this region, the activation energy no longer shows the strong linear dependence on the jump distance as observed in the higher-alkali-metal region.  $\Delta E_{\text{act}}$  increases asymptotically to a final value of  $\sim 0.75 \text{ eV}$  as  $x$  increases. This behavior suggests that this value may be the fundamental limiting energy barrier affecting the conduction mechanism. This result is in accordance to the Anderson-Stuart model,<sup>35</sup> where the activation energy ( $\Delta E_{\text{act}}$ ) is given by the sum of the strain energy ( $\Delta E_s$ ) and the Coulombic binding energy ( $\Delta E_b$ ) and are defined below:

$$\Delta E_{\text{act}} = \Delta E_s + \Delta E_b, \quad (6)$$

$$\Delta E_s = 4\pi G(r - r_D), \quad (7)$$

and

$$E_b = \frac{zz_0e^2}{\epsilon_\infty} \left[ \frac{1}{r+r_0} - \frac{2}{\alpha} \right]. \quad (8)$$

$G$  is the shear modulus of the glass;  $r_D$ ,  $r$ , and  $r_0$  are the interstitial window, the cation and the nonbridging anion radii, respectively,  $\alpha$  is the jump distance,  $z$  and  $z_0$  are the charges on the mobile cation and the nonbridging anion, and  $e$  is the charge on a electron. The variation in the shear modulus and  $\epsilon_\infty$  for these slightly different glass compositions may be best approximated as constants. The strain energy contribution to the activation energy is therefore expected to be a constant and fairly small, see Ref. 36 for calculations on Na<sub>2</sub>O+B<sub>2</sub>O<sub>3</sub> glasses. In the Coulombic energy equation, all the variables are constant except for  $\alpha$ . The line through the data in Fig. 13 is the activation energy calculated from the AS model. The trend is in good agreement with the experimental data and shows the rapidly diminishing influence of the jump distance for  $\alpha > 15 \text{ \AA}$ .

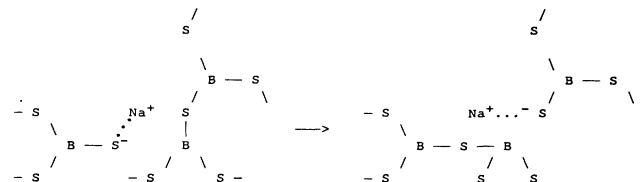
A question that arises from these results for dilute glass systems is what is an acceptable definition for the jump distance? The alkali-metal-alkali-metal separation distance has been used as the jump distance for alkali-metal concentrations greater than 0.02. It would seem that the asymptotic behavior of the conductivity activation energy in the low-alkali-metal suggests that whatever the energy barrier, it appears to remain constant. Some hint for the asymptotic value can be gained by returning to the Anderson-Stuart Eq. (6). The limit as  $\alpha$  goes to infinity for Eq. (6) is given below:

$$\lim_{\alpha \rightarrow \infty} \Delta E_{\text{act}} = \lim_{\alpha \rightarrow \infty} \Delta E_s + \lim_{\alpha \rightarrow \infty} \Delta E_b \quad (9)$$

$$= \lim_{\alpha \rightarrow \infty} \Delta E_s + \frac{zz_0e^2}{\epsilon_\infty} \left[ \frac{1}{r+r_0} \right] \quad (10)$$

$$= \text{Constant} + \frac{zz_0e^2}{\epsilon_\infty} \left[ \frac{1}{r+r_0} \right]. \quad (11)$$

Unfortunately, without values for the shear modulus  $G$  and the interstitial window radius  $r_D$ , accurate estimations are not possible. What these equations do suggest, however, is that the activation energy is one where the cation is not jumping into another cation site, but rather, into some type of defect site. Here if a cation were jumping into a near-neighbor site, then the  $\alpha^{-1}$  term would be active. The exact nature of the defect site, however, is unknown at this point. Perhaps one possibility would be for the jumping cation to cause bond interchange according to the reaction shown below:



This would require a cage activation energy, essentially that of the  $B-S$  bond strength. At the low-alkali-metal extreme where it is believed such processes may be taking place, the limiting activation energy is  $\sim 0.75$  eV (71 kJ/mol). This value is much smaller than the estimated  $B-S$  bond strength of 200–300 kJ/mol and suggests that if such a process is occurring, it must be a concerted one where bond breaking and reforming processes are acting simultaneously to lower the activation barrier. To answer these questions, we are presently performing molecular dynamics simulations to determine the actual jump distance and investigating the various possible cation environments in these low-alkali-metal glasses.<sup>37</sup>

#### IV. CONCLUSIONS

We report a thorough low to extremely low-alkali-metal composition studies of the effect of glass composition on the extent of nonexponentiality of conductivity relaxation. The transition from nonexponential to ex-

ponential relaxation in conductivity relaxation is reported for  $x(\text{Na}_2\text{S})+(1-x)\text{B}_2\text{S}_3$  composition glasses. Our results show that the  $\beta$  parameter in the Kohlrausch relaxation function correlates well with the alkali-metal–alkali-metal separation distance and strongly supports the hypothesis that ion-ion coupling is the reason for the conductivity dispersion in frequency.

The activation energy data plotted against the alkali-metal–alkali-metal jump distance show two distinct regions where different conductivity mechanisms are proposed to be active. At high-alkali-metal concentrations, the amount of overlap of potential energy wells between alkali-metal sites strongly affects the activation energy. At low-alkali-metal concentration, the effect due to overlap of energy wells is nonexistent and the activation energy is independent of jump distance. The data in both regions agree well with the Anderson-Stuart model. A possible model has been developed to explain the limiting behavior of the activation energy with concentration in the extreme dilute region.

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