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Nuclear-spin relaxation in ionically conducting glasses: Application of the diffusion-controlled relaxation model

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A theoretical mechanism for nuclear-spin relaxation in ionically conducting glasses (or disordered crystals) is proposed. This is based on the diffusion-controlled relaxation model previously used to account for electrical relaxation in such materials. In this model, ionic relaxation is assumed to occur at interstitial sites, triggered by the arrival of diffusing ions. The dependence of the spin-lattice relaxation rate on the temperature, Larmor frequency, and ionic concentration can all be understood with use of this model.

I. INTRODUCTION

Our understanding of ionic transport processes in disordered materials is still rather rudimentary and the atomic structure of amorphous materials, in general, is not known, particularly in relation to the (local) structural environment of the conducting ions. As a result, unlike the situation for *crystalline* ionically conducting materials, the conduction paths for ions are not known for amorphous solids and, hence, the microscopic ionic transport mechanism is unclear. This problem is compounded by the fact that experimental investigations of ionic transport, such as dc conductivity measurements as a function of temperature or (total) ion concentration N, do not provide direct information on the conduction process involved; this difficulty can only be tackled by making measurements on, say, the ionic mobility μ itself, for example, using the Hall effect,[1] whereby the influences on the ionic conductivity of possible changes in μ or the *mobile* ion concentration n with variations in temperature or N can be separately evaluated. In this way it should be possible to decide between various models for the ionic transport mechanism, such as those stressing the role played by the ionic carrier concentration n (for example, in the "weak-electrolyte" theory),[2] or the ionic mobility[3] or "defects" such as interstitialcies (for a review, see Ref. 4).

Recently, it has been emphasized that studies of the *dynamic* behavior of ionic transport processes in amorphous solids can shed additional light on this problem.[5-8] Such measurements include frequency-dependent (ac) conductivity, quasielastic neutron scattering (QENS), and nuclear magnetic resonance (NMR) spin-lattice relaxation rate, the latter being the subject of this paper. The goal is to formulate a microscopic model for the dynamic behavior so that the proposed mechanism accounts satisfactorily for the experimental results obtained from these three techniques, which encompass a very wide range of frequencies ($\simeq 10-10^{11}$ Hz).

Three models for ionic transport in disordered materials, based to a greater or lesser extent on a microscopic picture, have been proposed: these are the "diffusion-controlled relaxation" model proposed by the present authors,[7,9,10] the "jump-relaxation" model of Funke and co-workers [11-15] and the "coupling" model due to Ngai *et al.*[16-18] These will be reviewed briefly in the following sections as likely mechanisms for nuclear spin relaxation in ionically conducting glasses.

II. MODELS FOR DYNAMIC IONIC TRANSPORT BEHAVIOR IN GLASSES

A. Diffusion-controlled relaxation model

The diffusion-controlled relaxation (DCR) model assumes that ionic transport in (superionic) glasses occurs through the motion of interstitial defects and that the relaxation processes giving rise to the dispersive dynamic ion-transport behavior occur at the interstitial sites themselves;[7] the arrival of an ion at a site already occupied by an ion, thereby producing an interstitialcy, is presumed to result in a local structural rearrangement of the original ion, somewhat similar to, but distinct from, the process envisaged by Charles[19] (see Fig. 1). This mechanism, whereby relaxation is triggered by the arrival of an ion, is a process of "target diffusion" as originally envisaged by Glarum[20] except that, in the DCR model, the diffusing "defects" of the Glarum picture are the ions themselves. (The notion that ions could act as entities triggering relaxation events was also suggested, but not analyzed, earlier by Hodge and Angell.[21])

It should be noted that the DCR model has both series and parallel relaxation aspects. The series aspect arises from the fact that the relaxation is assumed to be dominated by the diffusion-triggering mechanism. Thus, interionic correlations, indisputably important in ionically conducting materials, occur explicitly in this model at the lowest level, i.e., pairwise at interstitial sites. (In addition, interionic correlations may also arise implicitly, for example, in determining the ionic diffusion coefficient, which is taken as a given parameter in the theory.) The parallel aspect of the DCR model is that the *total* relaxation response is assumed simply to be the sum over all individual relaxation events occurring *independently* at

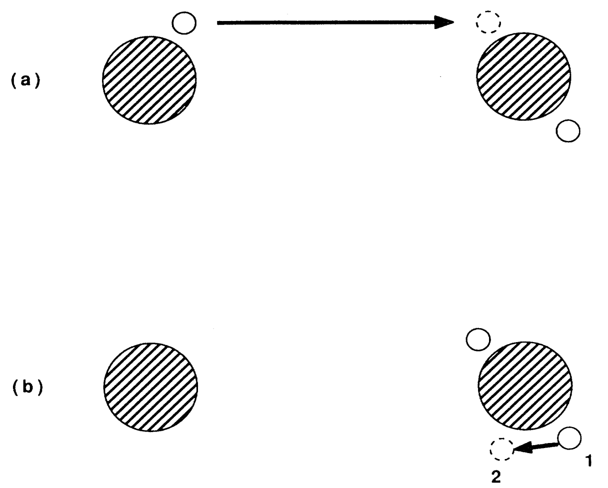

FIG. 1. Schematic illustration of the microscopic ionic relaxation process underlying the DCR model. A diffusing ion on arriving at an occupied site and thereby forming an interstitialcy (a), causes a local rearrangement (relaxation) of the original ion due to the mutual Coulombic repulsion between the two ions (b).

each interstitial site.

For this model, the temporal decay function describing the relaxation behavior after the abrupt removal of a steady exciting field (e.g., for electrical polarization) can be written as[9,10,22]

$$\phi(t)=c\exp(-t/\tau')\exp[-(t/\tau_3)^{1/2}] \tag{1}$$

for the case when *all* species (viz., ions), assumed to be randomly situated in space and diffusing in three dimensions, can act as triggering entities. Note that Eq. (1) predicts a stretched-exponential (Kohlrausch-Williams-Watts) behavior, albeit with a time-dependent exponent β.[10] At very long times, $t \gg \tau'^2/\tau_3$, pure exponential behavior ($\beta=1$) is recovered.[10] In Eq. (1), the two characteristic times τ' and τ_3 are given by

$$1/\tau'=1/\tau+4\pi DRn \tag{2}$$

and

$$1/\tau_3=64\pi DR^4n^2 , \tag{3}$$

where D is the diffusion coefficient of the ions, n is the concentration of (mobile) ionic species, R is the radius of the interstitial site (assumed to be constant) within which the relaxation event is supposed to occur, and τ (also assumed to be constant) is the characteristic relaxation time for the (exponential) relaxation decay occurring in the *absence* of diffusion-induced triggering arising, say, from the local motion of a single ion at a site due to thermal excitation from its stable position to another metastable position over an energy barrier W in a double-well potential (W is also, for simplicity, assumed to be constant from site to site). Finally, in Eq. (1) the parameter c is a constant, in the range $0<c<1$, given by the fraction of centers relaxing instantaneously at $t=0$ (due to triggering ions being already present inside the relaxation radius R at this time).

The degree of nonexponential (i.e., stretched) behavior predicted by the DCR model[10,23] is determined by the ratio $\tau'/\tau_3 \simeq 16R^3n$ (if the diffusion-independent term involving τ is neglected). Thus, exponential relaxation behavior is predicted to be recovered as the concentration of diffusing triggering ions tends to zero.[10] The reason for this is that an exponential relaxation decay is obtained when there is no influence on the probability of a site being relaxed due to the occurrence of previous diffusion-triggered relaxation events,[22] i.e., there is no correlation between relaxation events. This is believed to be the origin of the previously nonunderstood, experimentally observed[24] compositional dependence of the exponent β.

Three assumptions are made concerning the *structure* of the material in which this target-diffusion process is assumed to occur: the first is that interstitial sites with a (constant) radius R exist in the host structure, the second is that the diffusing ions are assumed to be distributed in a random fashion,[22] and the third is that the diffusion occurs on a regular, i.e., nonfractal (albeit noncrystalline) structural framework. In practice, there will be a distribution of sizes of interstitial sites; however, we have recently shown[25] that the size distribution of interstitial holes in a model of vitreous SiO_2 is, in fact, not very broad and so it may be surmised that the assumption of a fixed interstitial-site radius for a glass of a given composition is probably not unreasonable. Furthermore, the assumption that the diffusing ions are completely randomly distributed with respect to a target interstitial site is also reasonable, particularly for ion concentrations which are not too large. At high-ion concentrations, this assumption may begin to break down and a reasonably well-defined (nonrandom) nearest-neighbor ion-ion distance may begin to emerge. Hunt and Powles[26] have analyzed the behavior of the target-diffusion model in the case when the relaxation-triggering entities are distributed in such a nonrandom fashion and find, provided that a diffusion-independent exponential term is included in the relaxation function $\phi(t)$, that the behavior is predicted to be qualitatively very similar to that when the diffusing species are distributed randomly. The final assumption namely, that the diffusion takes place on a regular, albeit noncrystalline, structural framework, affects the value of the exponent β in the stretched-exponential functional form of the relaxation function $\phi(t)$. However, percolation clusters near criticality (e.g., ion-conducting channels) can exhibit *fractal* characteristics, and target diffusion on such structures leads to different values of the exponent β:[10] for values of the fracton (spectral) dimension $\tilde{d}<2$, the exponent takes the value $\beta=\tilde{d}/2$,[27,28] i.e., β can differ from the value of one-half.

A further assumption made in the DCR model[10] is the so-called "first-passage" approximation, whereby it is assumed that relaxation occurs *instantaneously* once a triggering entity (ion) arrives inside the relaxation radius R. This assumption leads to a finite jump in $\phi(t)$ at $t=0$ [c.f., the constant c in Eq. (1)] resulting from the instantaneous relaxation events caused by those triggering entities within the relaxation volume at $t=0$. This unphysical feature of the model has been dealt with recently by Condat[29] who showed that, if a *finite* rate of relaxation of a target by a diffusing triggering entity is assumed instead, the time-dependent decay at very short times becomes a simple, exponential form, smoothly changing to a stretched-exponential behavior at longer times. (This purely exponential relaxation-decay behavior at very short times would also correspondingly be manifested at very high frequencies, and there is indeed evidence from Brillouin scattering experiments of *mechanical* relaxation in superionic glasses[30,31] that the nonexponential behavior observed at lower frequencies disappears for frequencies in the GHz range.)

Furthermore, the DCR model assumes that the triggering entities (ions) make *uncorrelated* hops in their diffusive motion which leads to triggering of relaxation. In *three* dimensions, this type of motion serves to minimize any nonexponential relaxation behavior.[22] It is conceivable, however, that *correlated* jump diffusion could occur and this feature could easily be incorporated into the DCR model, for example, by using a suitable waiting-time distribution[10,32] in a continuous-time random-walk[33] picture of the problem.

Finally, it should be stressed that the nonexponential relaxation behavior predicted by the DCR model does *not* arise from the physical existence of a distribution of relaxation times, as suggested, for example, by Dyre,[34] amongst others (although formally any type of nonexponential behavior can always be expressed in terms of such a distribution). Rather, the nonexponential behavior arises from the "fractal time"[35] characteristic of target-diffusion processes.

B. Jump-diffusion model

Following an earlier suggestion by Schmalzried,[36] Funke and co-workers have recently proposed[11-15] that ionic conduction in solid materials can be understood in terms of a Debye-Hückel-Falkenhagen approach.[37-39] A given ion at a site A can move to a nearby vacancy at B by thermal activation over an energy barrier, if the motion is adiabatic. Once at B the ion will probably perform a return hop back to A (a correlated forward-backward hop) since, in this case, the activation barrier for the reverse motion B to A is substantially lower than from the (stable) position A to B; the probability that the ion is still at B at time t, not having performed a correlated backward hop, is $W(t)$, which is used to calculate various time-correlation functions. Interionic interactions are introduced into the model by assuming that all the ions surrounding the hopping ion relax (on a slower time scale than that of the hopping event itself) so that eventually the site B becomes the position of lowest potential energy; thus, the shape of the double-well potential characterizing the sites A and B changes with time. For simplicity, a simple exponential time dependence, $g(t)=\exp(-t/\tau)$, with a fixed relaxation time τ, has been chosen in the early development of the model to represent the time-dependent relaxation behavior of the surrounding ions.[12,13] (The effect of Coulomb interactions on the conductivity due to the hopping motion of ions has also been considered by Bunde *et al.*[40-41])

However, several deficiencies are apparent with this model. First, it is not clear how valid such an approach, based on the Debye-Hückel-Falkenhagen theory for *dilute* (liquid) electrolyte solutions, is for the case of ionic conductors containing large concentrations of ions. Furthermore, it seems implausible that a many-body relaxation process, such as that involved in the relaxation of all surrounding ions following an individual ion hop, should have a simple exponential time-dependent behavior for the relaxation decay. In fact, in more recent developments of the model, Funke[42-44] has relaxed the assumption of a simple exponential form for $g(t)$ and a more realistic derivation of $g(t)$ leads to a marked nonexponential character of this quantity, which can be represented approximately by a stretched-exponential function; although, at very short times, $g(t)$ always has a simple exponential form.[43] In addition, the jump-diffusion model predicts that, at very high frequencies, a frequency-*independent* behavior of the conductivity, viz. $\sigma(\infty)=\text{const}$, should occur,[12,13] however, there is no experimental evidence for the occurrence of such plateaus for ionically conducting glasses before the onset of phonon absorption bands at very high frequencies ($\sim 10^{12}$ Hz)—see, e.g., Ref. 45. In conclusion, the jump-diffusion model is likely to be applicable, if at all, to the case of *poorly* ionically conducting materials—e.g., oxides—where the mechanism of ionic transport is likely to involve discrete hopping events. It is not clear, however, that it should be applicable to the case of *superionic* glasses.

C. The coupling model

Ngai and co-workers[16,46] have long stressed the usefulness of representing the relaxation behavior in a wide variety of systems by a stretched-exponential, Kohlrausch-Williams-Watts (KWW) type temporal function. The basis of these ideas is the assertion that, at very short times, the rate of a particular (uncorrelated) relaxation process is constant, $W(t)=\tau_0^{-1}$, leading to an exponential time dependence, whereas, at times longer than a critical time t_c, owing to successively constraining correlations, the relaxation rate becomes time dependent with an assumed power-law time dependence, $W(t)\propto t^{-n}$ (where $0<n<1$); this leads to a stretched-exponential (KWW) form for the decay function, $\phi(t)=\exp[-(t/\tau^*)^{1-n}]$, $\beta=1-n$, where n (or β) is independent of time. In addition, a relation between relaxation times has been suggested,[16,46] viz,

$$\tau^*=[(1-n)]\omega_c^n\tau_0]^{1/(1-n)} , \tag{4}$$

where $\omega_c=1/t_c$. If τ_0 and τ^* are each thermally activated, with activation energies E_a and E_a^*, respectively, Eq. (4) implies that[16,46]

$$E_a=(1-n)E_a^* . \tag{5}$$

According to this approach, it is asserted that it is E_a, and not E_a^* (which is ascribed to the dc conductivity activation energy in the case of ionic transport), which is the true microscopic (primitive) activation energy for the relaxation process.

A serious shortcoming of this approach is that the parameters involved in the model, namely, n (or β), and τ^* and t_c (the time marking the crossover from exponential to stretched-exponential behavior) are *not* related microscopically to physical quantities involved in the particular relaxation process but, instead, are empirical fitting parameters. Furthermore, although the nonexponentiality is ascribed to interionic correlations in the case of ionic transport, the model does not provide a relationship linking the exponent n (or β) to the ionic composition, although if correlations are the determining factor, it is plausible[47] that n should tend to zero (or $\beta \rightarrow 1$—i.e., exponential behavior is recovered) in the limit of very low ionic concentrations, as observed.[24]

III. NUCLEAR-SPIN RELAXATION IN IONICALLY CONDUCTING GLASSES

A. Introduction

There has been considerable interest in measuring nuclear-spin-relaxation (NSR) rates, e.g., associated with spin-lattice relaxation, T_1^{-1}, of isotopes of atoms which, as ions, are mobile in glassy (or crystalline) hosts. The NSR behavior of such ions, say as a function of temperature, can give information on ionic transport processes in such materials. Martin[48] has recently given a review of the use of such techniques in the study of ionic transport in glasses. Thus, for example, Göbel *et al.*[49] and more recently, Balzer-Jöllenbeck *et al.*[50] have studied the NSR behavior of a variety of relatively poor ionically conducting oxide glasses (silicates, borates, germanates, and phosphates). Silver-containing oxide glasses, particularly incorporating so-called halide "doping salts" (e.g., AgI), exhibit considerably higher ionic conductivities than the corresponding alkali-metal oxide glasses. The NSR behavior of these materials has also been studied by a number of authors.[51–53] Sulphide glasses exhibit much larger (typically a thousandfold) ionic conductivities than the corresponding oxide materials having the same conducting-ion concentration,[54] and the NSR behavior of both alkali-metal-containing[55–59] and Ag-containing[59–60] thiosalts (e.g., thioborates, thiosilicates, and thiogermanates) have been investigated.

At sufficiently high temperatures (the upper limit being dictated by the glass-transition temperature), the temperature dependence of the spin-lattice relaxation rate T_1^{-1} exhibits a peak which is, in general, asymmetric in shape; in an Arrhenius plot, the effective activation energies for the high-and low-temperature sides of the peak are usually very different, the high-temperature value E_1 being comparable to that of the dc conductivity, E_σ, whereas the low-temperature value E_2 is considerably smaller, $E_2 = \alpha E_\sigma$, with $\alpha = 0.3-0.5$. Furthermore, the high-temperature side of the peak of T_1^{-1} versus inverse temperature is independent of frequency (or equivalently magnetic field) in the motional-narrowing limit; the low-temperature side, in contrast, is frequency dependent with an approximate power-law frequency dependence, $T_1 \propto \omega^m$, where m may be slightly sublinear[50] or somewhat superlinear,[58] but, in all cases, $0 < m < 2$. A larger range of the temperature-dependent behavior of the spin-lattice relaxation rate is manifested in more highly ionically conducting materials for which the correlation times are correspondingly smaller. At the lowest temperatures, say below 200 K, the temperature dependence of the spin-lattice relaxation rate T_1^{-1} becomes much weaker[49] and can be represented as a power law, $T_1^{-1} \propto T^n$, where n is slightly superlinear,[50] $1 < n < 1.3$.

Obviously a major contributory cause of NSR in ionically conducting glasses is the motion of the ions themselves; such ionic motion gives rise to fluctuating magnetic fields which can cause NSR *via* a variety of nuclear-spin interactions, e.g., chemical shift, dipolar, or quadrupolar. Thus, a proper understanding of the observed temperature (and frequency) dependence of T_1 can only be achieved *via* a knowledge of the underlying microscopic mechanism for the dynamic ionic behavior.

B. Models for NSR in ionically conducting glasses

A model for ionic-motion-mediated NSR was proposed by Bloembergen, Purcell, and Pounds[61] (BPP). In the case of relaxation mediated by dipole-dipole interactions, the spin-lattice relaxation (SLR) rate can be written as[62]

$$1/T_1 = C[J(\omega) + 4J(2\omega)] , \tag{6}$$

where $J(\omega)$ is the spectral density function corresponding to the time-dependent correlation of motion between interacting nuclei, given by the Fourier transform,

$$J(\omega) = \int_{-\infty}^{\infty} g(t) e^{i\omega t} dt , \tag{7}$$

and ω is the Larmor frequency, and C consists of constants such as the magnitude of the nuclear spin and the gyromagnetic ratio. In the case where NSR occurs *via* a quadrupolar mechanism, the SLR rate is still given by Eq. (6), but with a different constant C.[62] In the BPP model, the correlation function is simply assumed to be a pure exponential function,

$$g(t) = c \exp(-|t|/\tau) , \tag{8}$$

where c is a constant and τ is a characteristic correlation time. Thus, from Eq. (6), the SLR rate is given by[62]

$$\frac{1}{T_1} = c' \left[\frac{\tau}{1+\omega^2\tau^2} + \frac{4\tau}{1+4\omega^2\tau^2} \right] , \tag{9}$$

where c' is another constant. If the correlation time is assumed to be thermally activated, with an activation energy E_A, the BPP model correspondingly predicts that the peak of the SLR rate *versus* inverse temperature should be *symmetrical* with effective activation energies of $+E_A$ and $-E_A$ on the high- and low-temperature sides of the peak, respectively, in contrast with the asymmetric peaks commonly observed experimentally in glasses. Further, the SLR rate is predicted to be frequency independent on the high-temperature side, as observed experimentally, but proportional to ω^{-2} on the low-temperature side, at variance with experimental observation. Finally, it is not obvious why E_A should equal E_σ, the dc conductivity activation energy, as observed.

The discrepancy in activation energies between that of the ionic dc conductivity, E_σ, and E_2, that of the SLR rate on the low-temperature side (often all that is measurable, particularly for poorly conducting materials[49]) has long been contentious, and a number of proposals have been made to account for this difference. It has been suggested,[51] for instance, that the discrepancy arises because the dc conductivity is a measure of *long-range* ionic migration, whereas NMR line narrowing or SLR could be sensitive to more *short-range* ionic motions, for which the energetics of ionic transport would be expected to be different. More recently, it has been proposed[8,48,63,64] that the origin of the disparity in activation energies lies in the *frequency* dependence of the relaxation behavior. It is asserted that the low-temperature region of the SLR peak, corresponding to the condition $\omega\tau \geq 1$, is equivalent in behavior to the high-frequency region of the ionic conductivity which is itself frequency dependent and which has an experimentally observed weaker temperature dependence than the (dc) frequency-independent region of the conductivity for which $\omega\tau < 1$. Although it has been demonstrated explicitly,[59] from ac conductivity and SLR rate results measured at the *same* frequency (10 MHz) on the same material (Li_2S-SiS_2 and Ag_2S-GeS_2-AgI), that, indeed, E_2 and $E_\sigma(\omega)$ *are* the same within experimental error, this approach does *not,* in our view, resolve the problem of the difference in activation energies for SLR and dc conductivity as has been claimed,[8,48] but merely shifts the emphasis to the real question: What is the microscopic origin of the nonexponential relaxation behavior observed in both NSR and electrical studies?

Attempts have been made to account for the asymmetric peaks of $\ln T_1$ versus $1/T$ in terms of a distribution of correlation times, $g(\tau)$, presumed to arise because of the random nature of the glassy matrix. Thus, a distribution function corresponding to the empirical Cole-Davidson function[65] has been used to fit experimental SLR data for a variety of glassy systems, both poorly conducting oxides[49] and superionic sulphides.[48,55,57] Although reasonable fits can be obtained for a given material at a particular Larmor frequency, this approach does not seem to be able to fit well the SLR data taken at different frequencies.[58] Furthermore, there is no physical basis for using this, or any other, distribution function for the correlation times.

An empirical modification to the BPP function for the SLR rate has also been suggested,[58,66] viz,

$$\frac{1}{T_1} = C\left[\frac{\tau}{1+(\omega\tau)^{1+\alpha}} + \frac{4\tau}{1+(2\omega\tau)^{1+\alpha}}\right], \qquad (10)$$

which is of a similar functional form to the empirical formula suggested by Cole and Cole[67] in respect of dielectric relaxation. However, this approach also suffers from the fact that it is essentially an empirical fitting function, devoid of physical meaning; moreover, it does not predict the Larmor frequency dependence of T_1 observed experimentally.[58]

In a similar fashion, the empirical stretched-exponential (KWW) function, with constant exponent β, viz.,

$$\phi(t) = \exp[-(t/\tau)^\beta], \qquad (11)$$

has also been used to fit SLR data for a number of (superionic) glasses.[48,53] Again, reasonable fits to the experimental data can be achieved, but this approach suffers because no theoretical justification is given for the use of the empirical KWW function and the parameters involved (β,τ) have no microscopic meaning.

Recently, Balzer-Jöllenbeck *et al.*[50] have proposed an interpretation of NSR for mobile ionic species in (poorly) ionically conducting (oxide) glasses in terms of the coupling model of Ngai *et al.*[16–18,46] It is asserted that it is the *low-temperature* activation energy E_2 of the SLR rate which represents the true microscopic energy barrier to ionic motion and *not* the (larger) activation energy, $E_1 = E_\sigma$. The weak dependence of T_1 on the Larmor frequency, $T_1^{-1} \propto \omega^{-m}$, where $0.5 < m < 0.8$, observed in ionically conducting oxide glasses on the low-temperature side of the peak, is interpreted in terms of a process in which NSR is mediated by interactions with two-level systems (TLS) at *all* temperatures. At low temperatures ($T \lesssim 200$ K), the temperature dependence of the SLR rate in these ionic glasses is weak ($\propto T^{-\gamma}$, $0 < \gamma < 0.3$), and this behavior is very similar to that observed at similar temperatures in non-ion-containing glasses, such as B_2O_3, where NSR relaxation by TLS centers has been proposed.[68–71] At temperatures above 200 K, the temperature dependence of the SLR rate becomes thermally activated, and Balzer-Jöllenbeck *et al.*[50] ascribe this behavior to an ion hop associated with a TLS transition (of the host matrix). In this way, it is claimed that the frequency dependence of T_1 can remain weak, as observed, but the temperature dependence can be enhanced; the energy barrier to ionic motion is then equal to the low-temperature activation energy of the SLR rate in this interpretation.

However, this qualitative picture has several shortcomings. In the TLS model as originally applied to low-temperature thermal anomalies in glasses,[72,73] a broad *distribution* of barrier heights in the double-well potential of the TLS centers is needed to predict the observed thermal behavior. Kanert *et al.*[74,75] have, in fact, recently fitted the frequency and temperature dependence of the SLR rate, at low temperatures, in a Li_2O-LiF-B_2O_3 glass using such a distribution of barrier heights. However, at higher temperatures, where ionic motion is supposed to influence NSR and the temperature dependence of T_1 is stronger, it is not clear how the inclusion of such a distribution into the model would influence the predicted NSR behavior: Is the (low-temperature) activation energy of the SLR rate related to the width of the distribution, the maximum barrier height involved, or an average weighted to lower energies?[76] Furthermore, it is not at all clear how a mechanism for NSR involving excitation of TLS centers can be consistent with the "coupling" approach of Ngai *et al.*,[16–18,46] where many-body interactions are supposed to be the cause of nonexponential relaxation.

However, a mechanism for TLS mediated NSR involving ionic motion[50] is more likely to be valid for NSR of *network-forming* (i.e., nonmobile) atoms in an ionically conducting glass. Recently, Avogadro *et al.*[77] have investigated the SLR behavior of ^{11}B in the superionic glass AgI-Ag$_2$O-B$_2$O$_3$ and found qualitatively similar behavior to that observed for ^{109}Ag in the *same* system,[53] namely, a weak temperature dependence of T_1 at low temperatures and a much stronger temperature dependence at more elevated temperatures. However, in the case of the ^{11}B SLR data,[77] the activation energy E_1 for the SLR rate on the high-temperature side of the peak is *not* equal to that of the ionic dc conductivity E_σ, but is about half the value, whereas the corresponding high-temperature activation energies E_1 for ^{109}Ag SLR are in agreement with E_σ in the case of a KWW-type fit to the data.[53] Note that the values of E_1 for ^{109}Ag quoted by Avogadro *et al.*[77] and taken from Ref. 51, where they were obtained from a BPP-like fit, are considerably smaller (by a factor of 3) than those obtained by Chang *et al.*,[53] although these authors also found anomalously low values of E_1 if a BPP type of fit was employed. This discrepancy throws into doubt, therefore, the validity of the claim made by Avogadro *et al.*[77] that $E_1(\text{Ag})+E_1(\text{B})=E_\sigma$.

Very recently, the "jump-diffusion" model of Funke[12–15] has been used to fit NSR data for ionically conducting glasses,[42,53,58] and Funke and Wilmer[42] have proposed a relationship between the NMR spectral density function $J(\omega)$ [Eq. (7)] and the ac conductivity $\sigma(\omega)$ (both quantities being complex):

$$J(\omega)=\frac{\epsilon_0 T_0}{\epsilon_0 T_0 i\omega+T\sigma(\omega)}\ , \tag{12}$$

where the parameter T_0, representing a characteristic temperature of the ionic conductor, is given by

$$T_0=\frac{cq^2x_0^2}{6\epsilon_0 k_B} \tag{13}$$

and where c is the concentration of the mobile ions with charge q and x_0 is the hopping distance. Thus, the SLR rate and ac conductivity are related, in this model, by Eq. (6) together with Eq. (12).

Although Chung *et al.*[53] find that the fits to their SLR data for Ag$_2$O-AgI-B$_2$O$_3$ glasses using the jump-relaxation model are as good as those obtained using the empirical KWW formalism, nevertheless, the values of the characteristic relaxation times τ_∞ obtained from the former fits are between 2 and 3 orders of magnitude smaller than the period of the Ag$^+$-ion "rattling" motion in such glasses, implying that the correlated ionic jump mechanism of Funke[11–15] may not be applicable in such superionic glassy materials.

Finally, Schirmacher and Schirmer[78] have also proposed a model for NSR in ionically conducting glasses based on an activated, fixed-range ionic hopping mechanism,[79] which is formally somewhat similar to that proposed by Funke.[11–15] SLR data for a lithium borate glass have been fitted using this model assuming a constant (flat) distribution of hopping activation energies. However, agreement with the data is poor.

C. The diffusion-controlled relaxation model for NSR

Here we aim to show how the DCR mechanism for ionic relaxation[7,9,10] as outlined in Sec. II A, can provide a satisfactory, self-consistent model for NSR in ionic glasses, particularly those which are rather good ionic conductors. In fact, target-diffusion processes[20] have been proposed previously to account for non-BPP-like NSR behavior in a variety of materials, including molecular liquids[26] and polymers,[80,81] where the diffusing entities were taken to be "defects" of a rather ill-defined nature. However, with the exception of the passing suggestion of Hodge and Angell,[21] we know of no other work besides ours which identifies the triggering species as diffusing atoms or, as in the present case, ions and which has made a quantitative analysis of this situation. A preliminary account of the application of the DCR model to NSR in ionically conducting glasses has been given elsewhere.[23]

In analyzing the NSR of nuclei of mobile ionic species (e.g., Li$^+$, Ag$^+$) in a glassy matrix, we assume that the relaxation of a particular nucleus of an ion at a given site is caused by the fluctuating fields due to the diffusive motion of other ions, as in earlier work on diffusion-mediated NSR,[82] including the seminal work of Bloembergen *et al.*[61] In other words, NSR can only occur when a diffusing ion approaches another ion sufficiently close for the fluctuating fields to be large enough to induce relaxation, i.e., the process is inherently one of *target* diffusion and previous diffusion-mediated theories[61,82] which failed to take account of this fact are therefore incomplete.

In order to evaluate the SLR rate, it is necessary to calculate the spectral density function $J(\omega)$, related via Eq. (7) to the time-dependent correlation function $g(t)$ for the atomic motion. In this paper, we will use for $g(t)$ the solution due to Bordewijk[22] for target diffusion in three dimensions, where *all* diffusing species can act as triggering entities, as previously employed in a discussion of dielectric relaxation.[10] [Previously, Hunt and Powles used a three-dimensional (3D) generalization of the Glarum solution[20] where only nearest neighbors act as relaxation triggers, whereas Kimmich and Voigt[81] have considered a number of 3D diffusion situations similar to, but not the same as, that discussed by Bordewijk.[22]] Thus, except at very short times, where the correlation function is expected to transform smoothly to pure exponential behavior,[29] $g(t)$ is expected to be given by Eq. (1).

Note, however, that the microscopic identification of the radius R appearing in the expressions for the characteristic times τ' and τ_3 [Eqs. (2) and (3), respectively] in the case of NSR is *not* necessarily the same as that arising in the case of dielectric relaxation, where it has been identified with the radius of an interstitialcy site;[10] the fluctuating fields arising from diffusive ionic motion might be expected to cause nuclear relaxation at an ionic site at appreciably larger distances than that of the interstitial-site radius.

Use of Eq. (7), with Eq. (1) for $g(t)$, yields for the spectral density function for the DCR model:[23]

$$J(\omega)=2\,\mathrm{Re}\left\{\frac{\tau'}{(1-i\omega\tau')}-\frac{\tau'}{2}\left[\frac{\pi\tau'}{\tau_3}\right]^{1/2}\frac{1}{(1-i\omega\tau')^{3/2}}\exp\left[\frac{\tau'}{4\tau_3(1-i\omega\tau')}\right]\mathrm{erfc}\left[\left\{\frac{\tau'}{4\tau_3(1-i\omega\tau')}\right\}^{1/2}\right]\right\}, \tag{14}$$

where τ' and τ_3 are given by Eqs. (2) and (3), respectively. The real part of the complex expression for $J(\omega)$ can be separated by numerical means.[10] From this, the SLR rate, T_1^{-1} can be evaluated using Eq. (6).

It should be noted from Eq. (14) that the (complex) spectral density function and, hence, the SLR rate, can be regarded as the sum of two terms, the first of which, viz., $\tau'/(1-i\omega\tau')$, is simply the BPP expression;[61] the non-BPP-like behavior thus arises from the second correction term in Eq. (14). This correction term tends to zero, i.e., BPP-like behavior is recovered for two conditions: (i) for $\omega\tau' \ll 1$, so that the high-temperature, Larmor-frequency-independent region of the peak of T_1^{-1} versus $1/T$ (where $\omega\tau' \ll 1$) is unaffected by nonexponential NSR behavior and (ii) for $(\tau'/\tau_3)^{1/2} \rightarrow 0$. If the diffusion-independent term $1/\tau$ is neglected in Eq. (2) for τ' then, taken together with Eq. (3), the ratio τ'/τ_3 is proportional to the (mobile) ion concentration n:

$$\tau'/\tau_3 \approx 16R^3 n \ . \tag{15}$$

Thus, the non-BPP-like correction term to the SLR rate is predicted to become negligible as the ion concentration tends to zero. This behavior, viz., the recovery of BPP-like SLR behavior at very small ion concentrations, has recently been observed experimentally in lithium germanate glasses.[75] Similar behavior is also found for electrical relaxation in ionically conducting glasses, where Debye-like characteristics are recovered at very low ion concentrations.[24] The compositional dependence of the SLR rate will be discussed in more detail later in this section.

The DCR model also predicts an additive (non-Debye) term in the case of dielectric relaxation,[10] similar to that for the SLR rate [Eq. (14)]. It is worth noting here that Johari and Pathmanathan[83] have also suggested, on empirical grounds, that electrical relaxation data for ionically conducting glasses can be divided into two parts, one Debye-like and the other non-Debye-like; the former was presumed to arise from conductivity relaxation characterized by a single relaxation time, whereas the latter was presumed to result from dipolar reorientation processes having a distribution of relaxation times (e.g., as given by the empirical Cole-Davidson function[65]). This empirical procedure of Johari and Pathmanathan[83] has been shown to give better agreement with electrical modulus data at high frequencies; it should be noted, however, that the DCR model self-consistently predicts such additive behavior, although the interpretation of the Debye-like and non-Debye-like terms is completely different from that of Johari and Pathmanathan.[83]

Theoretical curves of the SLR rate versus inverse temperature calculated using the DCR model [Eqs. (6) and (14)] are shown in Fig. 2 for two choices of the ratio τ'/τ_3. It can be seen that, for nonzero values of τ'/τ_3, non-BPP-like behavior is manifested on the low-temperature side of the peak of SLR rate, viz., the effective activation energy there, E_2, is smaller than that, E_1, on the high-temperature side. In fact, the plot of T_1^{-1} versus inverse temperature is appreciably curved on the low-temperature side near the peak (as generally observed experimentally), and so it is difficult to deduce an accurate value for the effective activation energy E_2 from such a plot. Nevertheless, it is apparent that the extent of the non-BPP-like behavior predicted by the DCR model becomes greater the larger the value of the ratio τ'/τ_3.

Moreover, it should be noticed that, as the value of the ratio τ'/τ_3 is increased, the peak in the plot of SLR rate versus inverse temperature predicted by the DCR model is no longer coincident with that characteristic of the BPP solution [Fig. 2(b)]. This discrepancy is a manifestation of the fact that, when the non-BPP-like term in Eq. (14) is significant, the position of the peak in the SLR rate is no longer given by the condition $\omega\tau=1$, where ω is the Larmor frequency and τ is an effective correlation time. A similar result was found for the case of the loss peak in

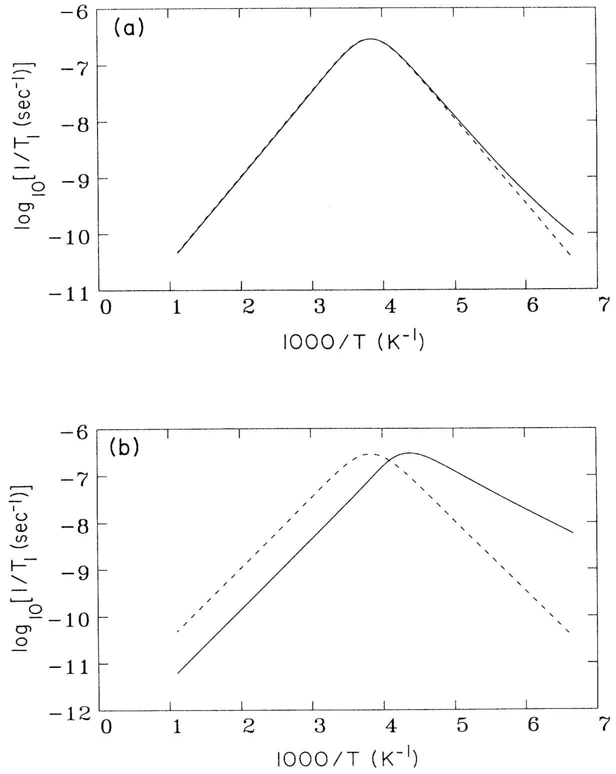

FIG. 2. Temperature dependence of the spin-lattice relaxation rate T_1^{-1} calculated for the DCR model for two choices of the ratio τ'/τ_3: (a) 0.02 and (b) 2.0. Note that non-BPP-like behavior is predicted for large values of this ratio. In both cases, a Larmor frequency of $\omega=100$ MHz and an (dc conductivity) activation energy $E_1=0.3$ eV have been used in the calculations.

dielectric relaxation,[10] and is, in fact, a general consequence of markedly nonexponential relaxation behavior.

In the present interpretation, E_2 has *no* physical meaning and the amount by which E_2 is less than E_1 is simply a manifestation of the degree of nonexponential behavior present in the NSR process due to the DCR mechanism. We therefore disagree with the interpretation of Balzer-Jöllenbeck *et al.*,[50] based on Ngai's coupling model,[16–18] that E_2 is the true microscopic activation energy. In our picture, it is E_1 (equal to E_σ) which is the microscopic activation energy.

Furthermore, the fact that the DCR model, as formulated in this paper, predicts (for small values of the ratio τ'/τ_3) a continuously decreasing temperature dependence of the SLR rate with decreasing temperature on the low-temperature side of the SLR peak, at least for, say, a four-decade change in the magnitude of T_1 from the peak maximum [Fig. 2(a)], which is as much as is commonly monitored experimentally, means that some (but not all) of the change in temperature dependence at low temperatures ascribed elsewhere to TLS-mediated relaxation[49,50] can thereby be accounted for. At the lowest temperatures, where the experimentally observed temperature dependence of the SLR rate is very weak,[49] the DCR mechanism can no longer be the dominant relaxation mechanism and some other mechanism (e.g., TLS-related) must intercede. Over a wide enough temperature range, i.e., for a sufficiently large range of values of T_1, the temperature dependence of the SLR rate predicted by the DCR model actually becomes accurately activated even for small values of the ratio τ'/τ'_3 with an activation energy E_2 considerably less than E_1 (in Fig. 3, for example, $E_2/E_1 \simeq 0.504$). (However, in practice, as mentioned above, this behavior would probably not be observed since it is likely that a TLS-related mechanism would be operative at the lowest temperatures.) It should be noted that in the model of SLR due to 3D defect diffusion studied by Kimmich and Voigt,[81] the ratio E_2/E_1 *always* has the value 0.5, independent of the parameters involved; it is a particular feature of the Bordewijk solution[22] of defect diffusion that the degree of nonexponential behavior, characterized by the ratio E_2/E_1 in the case of SLR, *is* dependent on certain parameters in the model such as, in our case, ion concentration.

In the DCR model for NSR, as formulated in this paper, the SLR rate on the high-temperature side of the peak (where $\omega\tau' \ll 1$) is determined by the first BPP-like term in Eq. (14); as a consequence, $T_1^{-1} \propto \tau'$ in this region. If the diffusion-independent term $1/\tau$ is neglected in Eq. (2), and if R and n are, moreover, assumed to be temperature independent,[10] then the temperature dependence of the SLR rate in the high-temperature region is governed by that of the diffusion coefficient since $\tau' \propto 1/D$ [Eq. (2)]. Furthermore, since $D \propto \sigma$, the DCR model for NSR predicts that the effective activation energy of the SLR rate on the high-temperature side of the peak is equal to that of the ionic dc conductivity, viz., $E_1 = E_\sigma$. This equivalence has been widely observed experimentally[48,53,57–59] and, although it is often stated[8,48] that it is physically plausible that E_1 should equal E_σ for those cases where ionic motion is responsible for NSR, the DCR model demonstrates this equivalence unequivocally in a theoretically self-consistent manner.

We now turn to a discussion of the dependence of the ionic-motion-mediated SLR rate on the concentration of (mobile) ions. Ngai *et al.*[47] and Kanert *et al.*[75,84] have investigated this behavior experimentally for a number of alkali germanate and aluminogermanate glasses, and typical results[75] for a series of lithium germanate glasses with differing lithium contents are illustrated in Fig. 4. It can be seen that, whilst E_σ decreases gradually with increasing mobile-ion content, as is well established from numerous studies of ionically conducting glasses (due presumably to changes in the structure and conducting pathways of the host glass), the SLR effective activation energy E_2 exhibits a much more rapid compositional variation, particularly at very low ion concentrations x, where $E_2 \rightarrow E_\sigma$; i.e., BPP-like behavior is recovered as $x \rightarrow 0$.

Qualitatively similar behavior is observed for *electrical* relaxation in ionically-conducting glasses: the stretched-

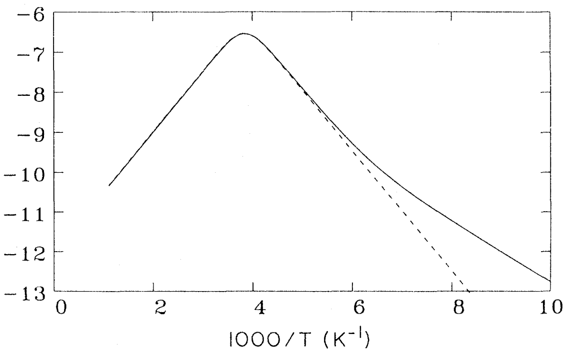

FIG. 3. Temperature dependence of the SLR rate for the DCR model with $\tau'/\tau_3 = 0.02$ for a more extended range of temperatures than shown in Fig. 2(a). (Other parameters are the same as those used in Fig. 2).

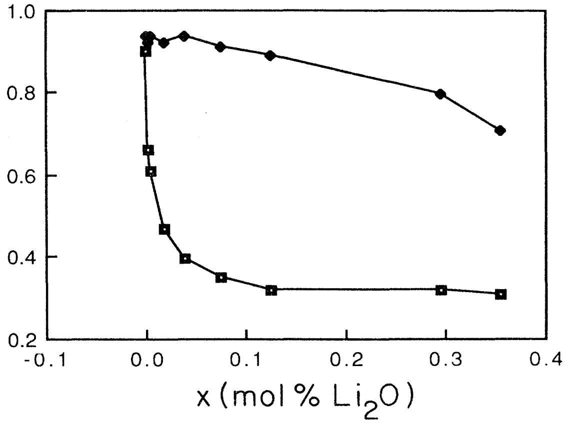

FIG. 4. Experimental activation energies for ionic conduction, E_σ (♦) and ^{7}Li NSR, taken from the low-temperature side of the peak of SLR rate, viz., E_2 (□), for various concentrations of lithia in the series of germanate glasses $(Li_2O)_x(GeO_2)_{1-x}$ (Refs. 75 and 84).

exponential exponent β, obtained from modulus data, tends to unity as the ion concentration tends to zero,[24,85] i.e., Debye-like relaxation behavior is recovered under such circumstances. Ngai *et al.*[47] and Martin[24] have pointed out that at very low ion concentrations, the interionic separation will be correspondingly very large and ion-ion correlations will then be minimized: these authors hypothesize that, under such circumstances, exponential relaxation behavior should be recovered, although no further theoretical justification nor a quantitative compositional dependence was given. It has been pointed out, however, that the DCR model for electrical relaxation[10] predicts such a compositional dependence of the non-Debye-like behavior.

The only quantitative expression for the composition dependence of SLR behavior previously given is that proposed by Kanert *et al.*[75,84] and Funke[86] based on a jump-relaxation model[12–15] incorporating Coulombic interactions between the hopping particles,[40,41] i.e., similar to the Debye-Hückel-Onsager treatment of dilute liquid electrolytes. On the basis of these considerations, the following relationship has been proposed:[75,84,86]

$$\frac{E_2}{E_1-E_2}=a\left[1+\frac{1}{K}\frac{E_2}{\sqrt{x}}\right], \tag{16}$$

where, as before, $E_1=E_\sigma$ and E_2 are the activation energies for the SLR rate on the high- and low-temperature sides of the peak, respectively, E_σ is the dc conductivity activation energy, x is the mole fraction of modifier (conducting-ion) oxide, a is a constant with a value of the order of unity, and the parameter K is given by the expression

$$K=3\left[\frac{e}{4\pi\epsilon_0\epsilon d}\right]^{3/2}, \tag{17}$$

where d is the mean hopping distance and ϵ is the dielectric constant of the glass. Note that since the ratio of activation energies for SLR and conductivity is found empirically from experiment[47] to be $E_2/E_\sigma=\beta$, where β is the exponent in the stretched-exponential function of the relaxation function, as predicted theoretically from Ngai's coupling model[47] as well as from the DCR model discussed in this paper, the left-hand side of Eq. (16) can therefore be rewritten as

$$\frac{E_2}{E_1-E_2}=\frac{\beta}{1-\beta}\ . \tag{18}$$

The SLR data for the $(Li_2O)_x(GeO_2)_{1-x}$ glasses shown in Fig. 4 are plotted according to Eq. (16) in Fig. 5 and, although it has been claimed[75,84,86] that the data fall on a straight line, in fact a rather pronounced curvature is evident in the plot. Furthermore, even less good agreement is exhibited if the data for the $(Na_2O)_x(GeO_2)_{1-x}$ glass system reported in Ref. 47 are plotted in a similar way. However, it should be remembered that it is often difficult to deduce reliable estimates for E_2 from plots of T_1^{-1} versus $1/T$ because, in many cases, the experimental SLR data do not fall exactly on a straight line. In fact, it is found that, if the SLR data for the Li_2O-GeO_2 glasses are plotted simply as $E_2/(E_1-E_2)$ versus $1/\sqrt{x}$, a better fit to a straight line than that obtained using Eq. (16) is achieved (see Fig. 5).

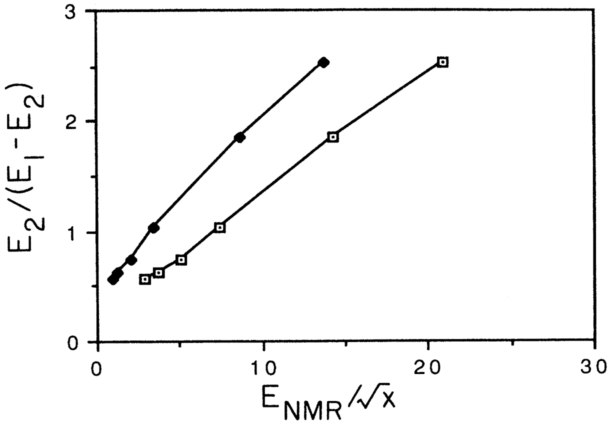

FIG. 5. SLR activation energy data (Refs. 75 and 84) for $(Li_2O)_x(GeO_2)_{1-x}$ glasses shown in Fig. 4 plotted according to Eq. (16) (◆) and also plotted simply vs the reciprocal of the square root of the ion concentration x (□).

The DCR model, based on the Bordewijk solution[22] for 3D diffusion also predicts a concentration dependence of the non-BPP-like SLR behavior observed in ionically conducting glasses, as for the non-Debye-like behavior of the electrical relaxation.[10] Examination of Eq. (14) for the spectral density function $J(\omega)$ predicted by the DCR model shows that, as mentioned previously, the magnitude of the non-BPP-like correction term for $J(\omega)$ and, hence, T_1^{-1}, is determined by the quantity $(\tau'/\tau_3)^{1/2}$. From Eqs. (2) and (3), if the diffusion-independent term $1/\tau$ is neglected in Eq. (2), then the parameter $(\tau'/\tau_3)^{1/2}\propto n^{1/2}$, where n is the mobile-ion concentration [Eq. (15)]. In other words, the DCR model also predicts that BPP-like behavior is recovered ($\beta\rightarrow 1$) as the ion concentration tends to zero, following a simple square-root law. It is expected from this consideration, therefore, that the quantity

$$E_2/(E_1-E_2)=\beta/(1-\beta)$$

might empirically obey a relationship somewhat similar to that of Eq. (16), namely

$$\frac{E_2}{E_1-E_2}=b\left[1+\frac{c}{\sqrt{x}}\right], \tag{19}$$

where b and c are constants. Note, however, that E_2 does *not* appear together with the concentration term on the right-hand side of Eq. (19) as it does in Eq. (16). This relationship exhibits the correct behavior at the two limiting concentrations: as $x\rightarrow 0$, $E_2\rightarrow E_\sigma$, and as $x\rightarrow\infty$, $E_2\rightarrow bE_\sigma/(1+b)$, i.e., a value appreciably less than E_σ.

Figure 6 shows a plot of values of $E_2/(E_1-E_2)$ calculated using the DCR expression for the SLR rate [Eqs. (6) and (14)] for varying values of the ratio τ'/τ_3, i.e., effectively the (mobile) ion concentration [Eq. (15)]. It can be seen that these calculated values do indeed fall ap-

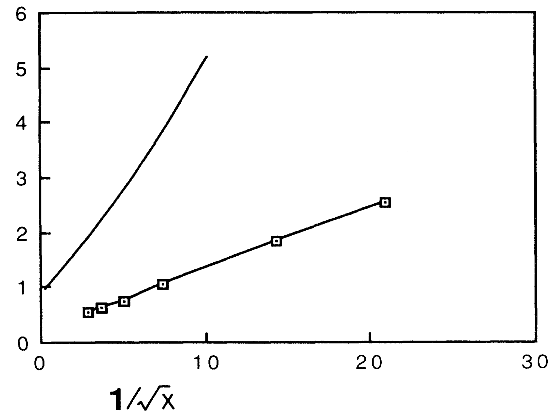

FIG. 6. Plot of $E_2/(E_1-E_2)$ calculated from the DCR model as a function of the ratio $(\tau'/\tau_3)^{1/2}$ (effectively the square root of the ion concentration x), represented as a continuous curve. The dc conductivity activation energy was chosen to be 0.92 eV [the average of the experimental values for the $(Li_2O)_x(GeO_2)_{1-x}$ system (Refs. 75 and 84)] and the Larmor frequency was taken to be $\omega=10$ MHz. Also shown are the (unscaled) experimental NSR data (Refs. 75 and 84) for glassy $(Li_2O)_x(GeO_2)_{1-x}$ plotted vs the reciprocal square root of the lithia concentration x (□).

proximately on a straight line in accordance with the empirical relationship expressed by Eq. (19), although it is apparent that the gradient of the plot decreases at the largest values of the ratio τ'/τ_3, i.e., at the largest ion concentrations. The infinite-concentration intercept (i.e., where $1/\sqrt{x}\rightarrow 0$) predicted for the DCR model is at a value

$$E_2/(E_1-E_2)=\beta/(1-\beta)\simeq 1 \ ,$$

i.e., the limiting value for the factor β (the exponent in the stretched-exponential factor) is $\beta=0.5$. This value is characteristic of NSR due to the DCR mechanism, e.g., as treated by Kimmich *et al.*[80,81]

Also shown in Fig. 6 are the experimental NSR data for glassy $(Li_2O)_x(GeO_2)_{1-x}$ as a function of the composition variable x. The DCR model is seen to exhibit qualitatively the same trend as the experimental data, but there is a difference in slope. However, there is a problem in reconciling the concentration scale for the experimental data and that of the ratio (τ'/τ_3) for the DCR model results on the abscissa. [No such difficulty exists for the ordinate in Fig. 6 since the quantity plotted, viz., effectively $\beta/(1-\beta)$, is independent of E_1.] This difficulty has two causes: one is due to the unknown value of the constant c in Eq. (19), and the other is associated with the uncertainty of the relation between the (experimental) *total* concentration of ions x and the (theoretical) concentration of *mobile* ions n, i.e., are all ions mobile? Considerably better agreement between the theoretical DCR results and the experimental data for $(Li_2O)_x(GeO_2)_{1-x}$ is obtained if the concentrations of the latter are multiplied by a constant factor of 14.8 to take account of the combined effect of the two uncertain features mentioned above (see Fig. 7). The (unscaled) SLR data for another alkali germanate glass,[47] namely, $(Na_2O)_x(GeO_2)_{1-x}$, are also shown in Fig. 7, whence it can be seen that these experimental data are in considerably better agreement with the theoretical predictions of the DCR model than are the raw lithium germanate data.

Another discrepancy between the lithium germanate data and the predictions of the DCR model, as developed so far in this paper, concerns the intercept on the ordinate as $1/\sqrt{x}\rightarrow 0$, as can be seen in Fig. 7. As mentioned above, a value of unity is expected from the DCR model (and indeed the sodium germanate data seem to behave in this way), but the experimental data for the lithium glasses tend towards an extrapolated intercept nearer a value of 0.25, implying the small limiting value of $\beta=0.16$, rather than the value of $\beta=0.5$ predicted by the DCR model. This discrepancy cannot be due to uncertainties in the scaling of the ordinate between experiment and theory, as mentioned previously. One possible explanation is that, for the case of the lithium germanate glasses, the ionic conduction takes place not on a regular "lattice" but, instead, on a *fractal* framework, for which values of $\beta<0.5$ can result for the DCR mechanism.[10] However, it is desirable that more experimental data be obtained on the ion-concentration dependence of the activation energies characteristic of NSR and dc conductivity in order to examine this point more carefully.

Finally, we discuss the dependence of T_1^{-1} on the Larmor frequency ω, particularly on the low-temperature side of the peak of SLR rate. On the high-temperature side of the peak of the SLR rate, i.e., where $\omega\tau \ll 1$, the DCR model predicts that T_1 is *independent* of the Larmor frequency, as in the BPP case. At lower temperatures, i.e., where $\omega\tau \gg 1$, the BPP model predicts that $T_1 \propto \omega^2$; this frequency-dependent behavior is observed, but only in certain *crystalline* ionic conductors.[62,76] In glassy ionic conductors (and some disordered crystalline

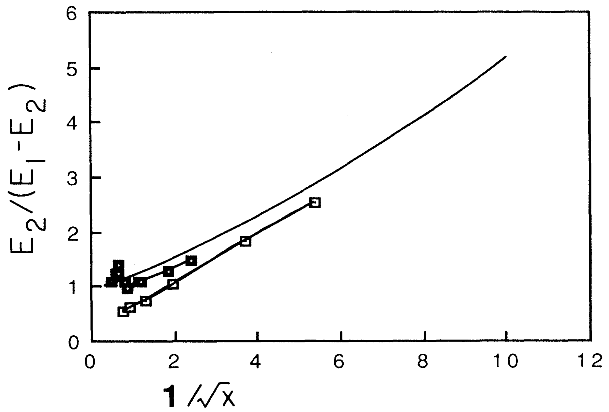

FIG. 7. A plot similar to Fig. 6 except that the experimental SLR data for the $(Li_2O)_x(GeO_2)_{1-x}$ glasses (□) have been rescaled by multiplying all concentrations by the factor 14.8. Also shown are the (unscaled) SLR data (Ref. 47) for $(Na_2O)_x(GeO_2)_{1-x}$ glasses plotted in the same way (■). The behavior predicted by the DCR model is again shown by the solid curve.

materials such as Na β-alumina), the frequency dependence of T_1 is considerably weaker than that predicted by the BPP model.

Owing to the relative difficulty of making Larmor frequency-dependent measurements using modern Fourier-transform spectrometers equipped with fixed-field superconducting magnets, a comprehensive investigation of the frequency-dependent behavior of NSR in ionically conducting glasses has not yet been performed. Nevertheless, on the basis of the presently available experimental evidence, it appears that, in relatively poor conducting (oxide) glasses (not containing doping salts), the frequency dependence is *sublinear,* $T_1 \propto \omega^{\gamma}$, $\gamma \simeq 0.8$, for all temperatures,[50] i.e., where TLS mediated NSR is believed to be dominant (at temperatures below 100 K) and also at higher temperatures where ionic motion is the dominant cause of NSR. Balzer-Jöllenbeck *et al.*[74] and Kanert *et al.*[75] have accounted for this behavior, at least at low temperatures where TLS involvement in NSR is important, by assuming that there exists a distribution of correlation times τ for the TLS excitations, where τ is given by[75]

$$\tau=\tau_0\,\mathrm{sech}(\Delta/2kT)\exp(V/kT)\ , \tag{20}$$

Δ is the asymmetry energy of the asymmetric double-well potential characterizing a TLS, and V is the barrier height separating the two minima (see Fig. 8); a distribution of τ results from an assumed distribution of barrier heights $g(V)$ presumably arising from the disordered nature of the host material. In this case, the SLR rate can be written as[75]

$$\frac{1}{T_1}=\delta\int_0^{\Delta_m}\int_0^{V_m}\frac{p(\Delta)g(V)}{\cosh^2(\Delta/2kT)}\,\frac{\tau}{(1+\omega^2\tau^2)}\,dV\,d\Delta\ , \tag{21}$$

where δ represents the strength of the TLS nucleus coupling, $p(\Delta)$ is the density of states of TLS centers, and Δ_m and V_m are the maximum values of Δ and V for the TLS states. For temperatures $T<V_m/k$, and using distribution functions for Δ and V, $p(\Delta)=\mathrm{sech}(\Delta/\Delta_0)$, and $g(V)=\mathrm{sech}(V/V_0)$, Eq. (21) leads to a power-law frequency dependence of the SLR rate, $T_1 \propto \omega^{\gamma}$, where the frequency exponent γ can have a value considerably less than the BPP value of 2, and even be sublinear, $\gamma<1$.[75]

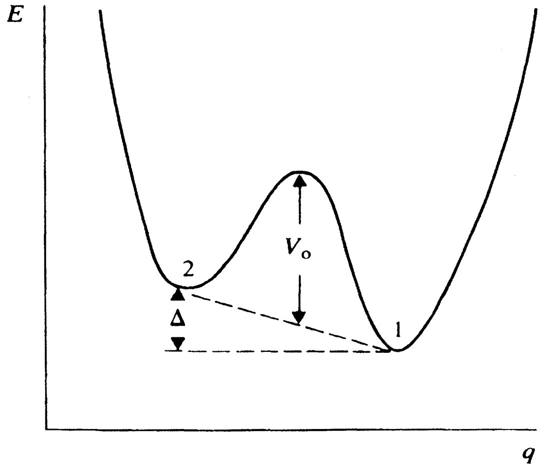

FIG. 8. Schematic illustration of the potential-energy diagram of an asymmetric double-well characterizing either a two-level system (TLS) or a local configuration of an ion at a site. The asymmetry energy Δ and the barrier height V are indicated.

In the case of the DCR mechanism for SLR in ionically conducting glasses as outlined in this paper, the frequency dependence of the SLR rate has a power-law behavior, $T_1 \propto \omega^{\gamma}$, where $\gamma=2-\beta$, and β lies in the range $0<\beta<0.5$ depending on the value of the ratio τ'/τ_3: the exponent β is given by the ratio of activation energies on the high- and low-temperature sides of the SLR peak, viz., $\beta=E_\sigma/E_2$. (Note that, in the case of the target-diffusion model for NSR developed by Kimmich and Voigt,[81] the exponent only takes the value $\gamma=1.5$.)

It appears from the limited experimental data available,[58] that *superionic* conducting glasses, e.g., Li^+- or Ag^+-conducting thiosalts or corresponding oxides containing doping salts, generally appear to have an appreciably enhanced power-law frequency dependence, with $\gamma=1.2-1.5$, compared with that for poor conducting ionic glasses.[50] This apparently qualitatively different behavior does not seem to have been remarked upon previously. Thus, in the SLR data presented by Grüne *et al.*,[58] the lithium thioborate glass $(\mathrm{Li_2S})_{0.46}(\mathrm{B_2S_3})_{0.54}$ exhibits a value $\gamma=1.5$, whereas the corresponding oxide $(\mathrm{Li_2O})_{0.46}(\mathrm{B_2O_3})_{0.54}$ has $\gamma=1.25$; likewise, for comparable materials containing doping salts,[58] the more highly conducting thiosalt $[(\mathrm{Li_2S})_{0.34}(\mathrm{B_2S_3})_{0.54}(\mathrm{Li_2Br_2})_{0.12}]$ has a larger frequency exponent ($\gamma=1.5$ again) than that of the corresponding oxide for which $\gamma=1.1$.

We assert that the NSR of these superionic glasses having Larmor frequency exponents of the SLR rate with values $\gamma\simeq1.5$ can be understood readily in terms of the DCR mechanism described in this paper [cf. Eqs. (6) and (14)]. Values of the frequency exponent $\gamma<1.5$ cannot be explained by the simple DCR model which assumes in Eq. (2), either a negligible diffusion-independent term $1/\tau$, or one which is constant.

However, in the case of diffusion-independent local ionic motion in an asymmetric double-well potential at a site, leading to relaxation, the NSR correlation time τ will be given by Eq. (20). In noncrystalline materials, a distribution of barrier heights $g(V)$ for such double-potential-well configurations will exist, as mentioned above, in the context of TLS centers. (It is important to stress, however, that the local ionic motion presently under discussion is *not* believed to be associated with the excitation of TLS centers,[50] operative at low temperatures, which almost certainly involves *many* atoms of the host glassy matrix and not just the conducting ions.) Since the double-well potential (see Fig. 8) associated with ionic relaxation is for the motion of *single* ions, the maximum barrier heights V_m are likely to be appreciably larger (say, $V_m\sim0.5$ eV) than those corresponding to the many-atom excitations giving rise to TLS states, where $V\sim5-10$ meV.[75] If the diffusion-independent term $1/\tau$ in the expression for the correlation time τ' [Eq. (2)] for the DCR mechanism of NSR is non-negligible, having, moreover, a broad distribution, then the DCR result for the SLR rate [cf. Eq. (14)] can be modified appropriately to take this into account. Hence, for example, the first-BPP-like correction term in Eq. (14) can be written in the form of Eq. (21), with the non-BPP-like correction term in Eq. (14) taking a more complicated modified form. In this way, it is anticipated that values of the Larmor frequency exponent γ of the SLR rate in the region of unity $(0.8 < \gamma < 1.2)$ could also be obtained from this extended version of the DCR mechanism of NSR; the temperature dependence of the SLR rate would still be thermally activated. Confirmation of this hypothesis awaits further work.

IV. CONCLUSIONS

In this paper, we have sought to show that the diffusion-controlled relaxation mechanism for ionic-motion-mediated relaxation in glasses can explain satisfactorily and self-consistently the nuclear-spin relaxation behavior experimentally observed in ionically conducting glasses, in particular, relating to spin-lattice relaxation. This model, a variant of a target-diffusion mechanism in which the diffusing triggering entities are the ions themselves, naturally predicts SLR behavior different from that predicted by the simple Bloembergen-Purcell-Pound model, viz., asymmetric peaks in plots of the SLR rate T_1^{-1} versus reciprocal temperature.

The model predicts that the effective activation energy obtained from the high-temperature region of such plots of SLR data (measured for the diffusing species) should equal that of the ionic diffusion coefficient or, equivalently, the dc ionic conductivity. The activation energy for the low-temperature side of the peak of the SLR rate is predicted to be generally appreciably smaller than that of the dc conductivity (reaching a limiting value of about one-half this value). The non-BPP-like behavior is predicted to be composition-dependent, varying as the square root of the mobile-ion concentration. The SLR rate is predicted to be independent of the Larmor frequency on the high-temperature side of the peak of the SLR rate, and to have a weaker power-law frequency dependence on the low-temperature side than that predicted by the BPP model, with the frequency exponent γ having the limiting value of 1.5. This theoretical behavior is in accord with that observed experimentally in *superionic* glasses, and the NSR in this case is ascribed to the DCR mechanism. For more poorly ionically conducting glasses (i.e., oxides), the values of γ are found experimentally to lie near unity, and this behavior can be accounted for by assuming that an additional diffusion-independent term is present in the expression for the correlation time, resulting from local ionic motion (hopping) at a site causing NSR; if the energetics of this hopping motion are assumed to be characterized by an asymmetric double potential well for which a distribution of barrier heights exists, it is anticipated that the near-linear Larmor frequency dependence of the SLR rate can be explained.

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[1] V. Clément, D. Ravaine, C. Desportes, and R. Billet, Solid State Ionics **28-30**, 1572 (1988); A. Denoyelle, M. J. Duclot, and J. L. Souquet, Phys. Chem. Glasses **31**, 98 (1990).

[2] D. Ravaine and J. L. Souquet, Phys. Chem. Glasses **18**, 27 (1977).

[3] O. L. Anderson and D. A. Stuart, J. Am. Ceram. Soc. **37**, 573 (1954).

[4] M. D. Ingram, Phys. Chem. Glasses **28**, 215 (1987).

[5] C. A. Angell, Solid State Ionics **18-19**, 72 (1986).

[6] S. W. Martin and C. A. Angell, J. Non-Cryst. Sol. **83**, 185 (1986).

[7] S. R. Elliott, Solid State Ionics **27**, 131 (1988).

[8] C. A. Angell, Chem. Rev. **90**, 523 (1990).

[9] S. R. Elliott, Mat. Sci. Eng. B **3**, 69 (1989).

[10] S. R. Elliott and A. P. Owens, Philos. Mag. B **60**, 777 (1989).

[11] K. Funke and I. Riess, Z. Phys. Chem. Neue Folge **140**, 217 (1984).

[12] K. Funke, Solid State Ionics **18-19**, 183 (1986).

[13] K. Funke, Z. Phys. Chem. Neue Folge **154**, 251 (1987).

[14] K. Funke, Solid State Ionics **28-30**, 100 (1988).

[15] K. Funke, in *Superionic Solids and Solid Electrolytes (Recent Trends)*, edited by A. L. Laskar and S. Chandra (Academic, New York, 1989), p. 569.

[16] K. L. Ngai, Comments Solid State Phys. **9**, 127 (1979); **9**, 141 (1980).

[17] K. L. Ngai, A. K. Rajagopal, and S. Teitler, J. Chem. Phys. **88**, 5086 (1988).

[18] K. L. Ngai and R. W. Rendell, Phys. Rev. B **38**, 9987 (1988).

[19] R. J. Charles, J. Appl. Phys. **32**, 1115 (1961).

[20] S. H. Glarum, J. Chem. Phys. **33**, 639 (1960).

[21] I. M. Hodge and C. A. Angell, J. Chem. Phys. **67**, 1647 (1977). The authors are grateful to Dr. Hodge for bringing this reference to their notice.

[22] P. Bordewijk, Chem. Phys. Lett. **32**, 592 (1975).

[23] S. R. Elliott and A. P. Owens, J. Non-Cryst. Solids (to be published).

[24] S.W. Martin, Appl. Phys. A **49**, 239 (1989).

[25] S. L. Chan and S. R. Elliott, Phys. Rev. B **43**, 4423 (1991).

[26] B. I. Hunt and J. G. Powles, Proc. Phys. Soc. London **88**, 513 (1966).

[27] J. Klafter and A. Blumen, Chem. Phys. Lett. **119**, 377 (1985).

[28] J. Klafter and M. F. Shlesinger, Proc. Natl. Acad. Sci. USA **83**, 848 (1986).

[29] C. A. Condat, Z. Phys. B **77**, 313 (1989).

[30] L. Börgesson, L. M. Torrell, S. W. Martin, C. Liu, and C. A. Angell, Phys. Lett. A **125**, 330 (1987).

[31] L. Börgesson, Phys. Rev. B **36**, 4600 (1987).

[32] M. F. Shlesinger and E. W. Montroll, Proc. Natl. Acad. Sci. USA **81**, 1280 (1984).

[33] H. Sher and E. W. Montroll, Phys. Rev. B **12**, 2455 (1975).

[34] J. Dyre, J. Appl. Phys. **64**, 2456 (1988).

[35] M. F. Shlesinger, Annu. Rev. Phys. Chem. **39**, 269 (1988).

[36] H. Schmalzried, Z. Phys. Chem. Neue Folge **105**, 47 (1977).

[37] P. Debye and E. Hückel, Phys. Z. **24**, 185 (1923); **24**, 305 (1923).

[38] L. Onsager, Phys. Z. **27**, 388 (1926); **28**, 277 (1927).

[39] P. Debye and H. Falkenhagen, Phys. Z **29**, 121 (1928); **29**, 401 (1928).

[40] A. Bunde, D. K. Chaturvedi, and W. Dieterich, Z. Phys. B **47**, 209 (1982).

[41] A. Bunde and W. Dieterich, Phys. Rev. B **31**, 6012 (1985).

[42] K. Funke and D. Wilmer, Europhys. Lett. **12**, 363 (1990).

[43] K. Funke and R. Hoppe, Solid State Ionics **40-41**, 200 (1990).

[44] K. Funke, Mater. Res. Symp. Proc. **135**, 43 (1989).

[45] A. Burns, G. D. Chryssikos, E. Tombari, R. H. Cole, and W. M. Risen, Phys. Chem. Glasses **30**, 264 (1989).

[46] K. L. Ngai, R. W. Rendell, A. K. Rajagopal, and S. Teitler, Ann. NY Acad. Sci. **484**, 150 (1986).

[47] K. L. Ngai, J. N. Mundy, H. Jain, O. Kanert, and G. Balzer-Jöllenbeck, Phys. Rev. B **39**, 6169 (1989).

[48] S. W. Martin, Mat. Chem. Phys. **23**, 225 (1989).

[49] E. Göbel, W. Müller-Warmuth, H. Olyschlager, and H. Dutz, J. Magn. Reson. **36**, 371 (1979).

[50] G. Balzer-Jöllenbeck, O. Kanert, H. Jain, and K. L. Ngai, Phys. Rev. B **39**, 6071 (1989).

[51] S. W. Martin, H. J. Bischof, M. Mali, J. Roos, and D. Brinkmann, Solid State Ionics **18-19**, 421 (1986).

[52] M. Villa, G. Chiodelli, A. Magistris, and G. Licheri, J. Chem. Phys. **85**, 2392 (1986).

[53] S. H. Chung, K. R. Jeffrey, J. R. Stevens, and L. Börgesson, Phys. Rev. B **41**, 6154 (1990).

[54] M. Ribes, D. Ravaine, J. L. Souquet, and M. Maurin, Rev. Chem. Min. **16**, 339 (1979).

[55] J. Senegas and J. Olivier-Fourcade, J. Phys. Chem. Solids **44**, 1033 (1983).

[56] S. J. Visco, P. Spellane, and J. H. Kennedy, J. Electrochem. Soc.: Electrochem. Sci. Tech. **132**, 751 (1985); **132**, 1766 (1985).

[57] A. Pradel, M. Ribes, and M. Maurin, Solid State Ionics **28-30**, 762 (1988).

[58] M. Grüne, H. Meierkord, W. Müller-Warmuth, P. zum Hebel, B. Krebs, and M. Wulff, Ber. Bunsenges. Phys. Chem. **93**, 1313 (1989).

[59] A. Pradel and M. Ribes, J. Non-Cryst. Solids (to be published).

[60] J. Roos, D. Brinkmann, M. Mali, A. Pradel, and M. Ribes, Solid State Ionics **28-30**, 710 (1988).

[61] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[62] D. Wolf, *Spin Temperature and Nuclear Spin Relaxation in Matter* (Clarendon, Oxford, 1979).

[63] C. A. Angell, Solid State Ionics **18-19**, 72 (1986).

[64] C. A. Angell and S. W. Martin, Symp. Mat. Res. Soc. **135**, 63 (1989).

[65] D. W. Davidson and R. H. Cole, J. Chem. Phys. **19**, 1484 (1951).

[66] C. Ritter, W. Müller-Warmuth, and R. Schöllhorn, J. Chem. Phys. **83**, 6130 (1985).

[67] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

[68] J. Szeftel and H. Alloul, Phys. Rev. Lett. **34**, 657 (1975).

[69] M. Rubinstein, H. A. Resing, T. L. Reinecke, and K. L. Ngai, Phys. Rev. Lett. **34**, 1444 (1975).

[70] T. L. Reinecke and K. L. Ngai, Phys. Rev. B **12**, 3476 (1975).

[71] M. Rubinstein and H. A. Resing, Phys. Rev. B **13**, 959 (1976).

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

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

[74] G. Balzer-Jöllenbeck, O. Kanert, J. Steinert, and H. Jain. Solid State Commun. **65**, 303 (1988).

[75] S. Estalji, O. Kanert, J. Steinert, H. Jain, and K. L. Ngai, Phys. Rev. B **43**, 7481 (1991).

[76] P. M. Richards, in *The Physics of Superionic Conductors,* edited by M. B. Salomon (Springer-Verlag, Berlin, 1979), p. 141.

[77] A. Avogadro, F. Tabak, M. Corti, and F. Borsa, Phys. Rev. B **41**, 6137 (1990).

[78] W. Schirmacher and A. Schirmer, Solid State Ionics **28-30**, 134 (1988).

[79] W. Schirmacher, Solid State Ionics **28-30**, 129 (1988).

[80] R. Kimmich, Z. Naturforsch. A **31**, 693 (1976).

[81] R. Kimmich and G. Voigt, Z. Naturforsch. A **33**, 1294 (1978).

[82] H. C. Torrey, Phys. Rev. **92**, 962 (1953).

[83] G. P. Johari and K. Pathmanathan, Phys. Chem. Glasses **29**, 219 (1988).

[84] S. Rückstein, O. Kanert, H. Jain, and K. Funke, Radiat. Eff. Defects Solids (to be published).

[85] K. L. Ngai and S. W. Martin, Phys. Rev. B **40**, 10 550 (1989).

[86] K. Funke, Radiat. Eff. Defects Solids (to be published).