JOURNAL OF CHEMICAL PHYSICS VOLUME 116, NUMBER 8 22 FEBRUARY 2002

New model for nearly constant dielectric loss in conductive systems: Temperature and concentration dependencies

J. Ross Macdonald[a)]
Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27599-3255

(Received 31 August 2001; accepted 21 November 2001)

By appropriate fitting of conductive-system frequency-response data for two different ionic materials over ranges of temperature and ionic concentration, it is shown how dispersion associated entirely with ionic motion and that leading to nearly constant dielectric loss (NCL) can be unambiguously distinguished and separated. The latter is clearly associated with polarization of the bulk material, and in the limit of zero mobile-ion concentration NCL appears to approach zero, yielding only a bulk dielectric constant, $\varepsilon_{D\infty 0}$, one that is frequency-independent over the usual immittance-spectroscopy experimental range. For nonzero ionic concentration, however, dielectric NCL appears and can be represented by a small-exponent constant phase element (CPE) complex power law in frequency. This part of the full response may be modeled either by a CPE that includes all bulk dielectric dispersion or, more plausibly, by $\varepsilon_{D\infty 0}$ and a CPE representing only incremental bulk dispersion associated with coupling between ionic motion and bulk polarization. In this case, interestingly, precise power-law dependencies of various dielectric parameters on ionic concentration are established but need theoretical explanation. Fitting of the ionic part of the total dispersion with three different Kohlrausch–Williams–Watts models leads to dependencies of their different β-shape parameters and dielectric quantities on temperature and on ionic concentration and strongly suggests that the widely used original-modulus-formalism dispersion fitting model is incorrect and should be replaced by a corrected version.
[DOI: 10.1063/1.1434953]

I. INTRODUCTION

An important outstanding problem in immittance spectroscopy is the nature of nearly constant dielectric loss (NCL) in conductive systems such as glasses with mobile charge carriers. Characteristic behavior is that where the dielectric loss function, $\varepsilon''(\omega)$, or a component of it, is a very slowly decreasing function of ω, usually of power-law form.[1–3] In some temperature-frequency regions, such loss is dominant, in others it can be identified as an important secondary part of the response, and in others it may not be resolvable.[4] Ngai, who has recently reviewed the NCL situation in detail, characterizes NCL, or apparent constant loss (CL), as ubiquitous in ion conducting glasses, melts, and crystals and characterizes it as a spectacular phenomenon.[5]

Ngai has also suggested that NCL may originate from a fundamental mechanism in condensed matter and that for ionic conductors it ‘‘originates principally from some local motion or vibrational degrees of freedom of the mobile ions.’’[5] The present work clearly indicates that, for the alkali glass data analyzed here, NCL is not directly associated with the effective high-frequency-limiting dielectric constant arising directly from ionic motion, $\varepsilon_{C1\infty}$. Instead, the presence of ions leads to an increment in the high-frequency-limiting dielectric constant of the bulk material, $\varepsilon_{D\infty}$, an increment that thus depends indirectly on ionic concentration. Because the data fitting suggests that the NCL effect is dielectric in character, it is then in parallel electrically with conductive-system ionic response, contrary to recent conclusions of Leon *et al.* in Ref. 4, further discussed in Sec. V below.

The coupling between ionic motion and dielectric polarization evident in the present results needs detailed theoretical analysis and is different from that of the Ngai coupling theory[6,7] and from the Funke theory of mismatch and relaxation.[8,9] On the other hand, it may possibly be related to the qualitative concept of correlated states discussed in Ref. 5. The total high-frequency-limiting dielectric constant is $\varepsilon_\infty \equiv \varepsilon_{C1\infty} + \varepsilon_{D\infty}$.

In the present work, the temperature and ion-concentration dependencies of significant parameters of various dispersion models used to fit immittance data for two different ionic materials are estimated by complex nonlinear least squares fitting (CNLS) of the data. Such fitting has been carried out using the LEVM computer program.[10] Different models are compared in order to show their appropriateness, or lack thereof, and to support and quantify the present NCL explanation. Most of the present fitting has involved proportional weighting (PWT).[10]

II. DATA-FITTING MODELS

The main models employed here are types of Kohlrausch–Williams–Watts ones.[11] Let us distinguish them using an index k. Then they may be denoted by KWWk, here simplified as Kk.[3,12–15] The most conventional model is the $k=0$ KWW0 one, or K0. Its frequency response corresponds,

---

[a)] Telephone: (919) 967-5005. Electronic mail: macd@email.unc.edu

through a Fourier transform, to stretched-exponential temporal behavior and involves the shape parameter $\beta_k = \beta_0$, the stretched-exponential exponent, with $0 < \beta_0 \leqslant 1$. When it is alternatively used to represent dielectric dispersion at the complex dielectric level, rather than resistivity dispersion, we set $k = D$. K0 is also the basis of the two other KWW models used herein,[12–15] and, although no analytical expressions for their frequency responses are available for arbitrary β values, LEVM allows all KWW models to be used for fitting or simulating frequency response or temporal data with a relative accuracy usually better than 10^{-5}.

In 1972–1973 the original modulus formalism (OMF) conductivity-relaxation approach was published, and it was first shown there how the K0 response model could be transformed to an important new one, the K1,[16,17] although these distinctions were not made at that time. Since then, the OMF has been widely used up to the present (e.g., see the 20 references to it listed in Ref. 18), even though crucial defects in it were pointed out in 1996[12,19] and a new version of it, the corrected modulus formalism (CMF), was introduced. Unlike the K0 and many other dispersion models, K1 response involves a dielectric constant contribution, $\varepsilon_{C1}(\omega)$, that can be shown to arise entirely from mobile charges and whose high-frequency limit, $\varepsilon_{C1}(\infty) \equiv \varepsilon_{C1\infty}$, is nonzero.[12,14,19]

Although the OMF dealt primarily with modulus response, $M(\omega) = 1/\varepsilon(\omega)$, it introduced a high-frequency-limiting dielectric constant, there denoted ε_S, an integral part of the conductive-system dispersion. This quantity was identified as containing "all the ordinary contributions to the relative permittivity of the material except those connected with the long range ionic diffusion process."[16] It was further noted that "... ε_S contains contributions from deformation and vibration losses and from the electronic polarization of the material, but no contributions from migration losses."[16] These definitions imply that ε_S represents the present bulk $\varepsilon_{D\infty}$ quantity, although in more recent work it has been identified with ε_∞ (e.g., Refs. 5, 6, and 18).

Both of the above definitions of ε_S are inapplicable because the K1 $\varepsilon_{C1}(\omega)$ expression, and therefore $\varepsilon_{C1\infty}$, arise entirely from mobile-ion effects and thus should not include any bulk ones. For actual data in cases where the ion-bulk coupling identified in the present work is appreciable, one might expect that the changes in $\varepsilon_{D\infty}$ might themselves affect $\varepsilon_{C1\infty}$, but any such changes are likely to be negligible. Note that although one expects that when $\varepsilon_{C1}(\omega)$ approaches and reaches $\varepsilon_{C1\infty}$, ions will be executing local librational motion, such dipolarlike effects involve the ions rather than the bulk-material surrounding network. Although both the OMF approach and the CMF one[12,14,15,19] involve the K1 model, they differ in two important respects. The first is the consistent use of the ion-only derived $\varepsilon_{C1\infty}$ quantity in the CMF and its replacement by the composite ion-bulk quantity ε_∞ in the OMF. The second is the need to include a separate parallel $\varepsilon_{D\infty}$ free parameter in fitting with the CMF K1 model. No such parameter is used or needed in the OMF, since that approach already implicitly or explicitly includes all $\varepsilon_{D\infty}$ effects through ε_S. When a free $\varepsilon_{D\infty}$ parameter is included in K1 fitting, the resulting CMF composite model will be designated by CK1.

There are three free parameters in the OMF K1 model and four in the CK1 CMF K1 one. The K0 model again requires a free dielectric parameter, this time representing ε_∞, and it will then be designated as the CK0. In addition, there are situations where a series or parallel power-law constant-phase-element (CPE) response function needs to be made a part of a composite-fitting model.[3,13,15] A series element, the SCPE, possibly representing electrode effects, is best defined at the complex resistivity level and may be written as $\rho_{\mathrm{SC}}(\omega) \equiv 1/[\varepsilon_V A_{\mathrm{SC}}(i\omega)^{\gamma_{\mathrm{SC}}}]$, where ε_V is the permittivity of vacuum and A_{SC} is a pure dielectric element when $\gamma_{\mathrm{SC}} = 1$. Similarly, a parallel CPE element, the PCPE, may be expressed as $\varepsilon_{PC}(\omega) \equiv A_{PC}(i\omega)^{-\gamma_{PC}}$, where A_{PC} is a pure dielectric element when $\gamma_{PC} = 0$. The combination of a K1 response model and a SCPE will be denoted as K1S, and that of a PCPE and a K1 as PK1. Both combinations involve five parameters.

It has recently been shown that either the CS or the PC model can lead to small-exponent power-law response for the corresponding $\varepsilon'(\omega)$ response and to apparent CL response for $\varepsilon''(\omega)$.[3] But the more common NCL response, involving small-exponent power-law behavior for both parts of $\varepsilon(\omega)$, can be modeled with such a combination as PK1 or PK1S.[3] There are seven parameters involved in the PK1S model, and when $\gamma_{PC} = 0$ it reduces to the CK1S model involving six free parameters. The CK0S model also involves six parameters. Of the composite models discussed here, the PK1S and CK1S ones have usually been found to be the most appropriate when the data involve a frequency range sufficient to allow statistically significant estimates of all their parameters to be obtained. Finally, it is worth emphasizing that the $\sigma'_C(\omega)$ response associated with the continuous-time random walk microscopic hopping theory of Scher and Lax[20] agrees closely in form with that of the macroscopic $\sigma'_{C1}(\omega)$ K1 model.[14,15,21] Such detailed agreement thus provides further theoretical justification for the appropriateness and effectiveness of CMF K1 models in data fitting.

III. TEMPERATURE DEPENDENCE

Table I lists some of the results of fitting single-crystal $0.88\mathrm{ZrO_2} \cdot 0.12\mathrm{Y_2O_3}$ data covering a range from about 20 Hz to 10^6 Hz. These data sets were kindly sent to me by Dr. C. León and form a part of a larger group of data on $\mathrm{ZrO_2{-}Y_2O_3}$ solid solutions,[22] ones that exhibit ionic conductivity. There is, however, no significant overlap between the present work and that in Ref. 22. The quantity $\mathrm{S_F}$ is the relative standard deviation of the fit residuals. Values of the order of 0.01 or less indicate an excellent fit, while those of 0.1 or more a poor fit. The OMF K1 fits of the $M''(\omega)$ data with unity weight [UWT] emphasize the fit to the largest values and thus yield estimates of the β_1 shape parameters close to those that would be obtained from the OMF procedure involving the full width of the $M''(\omega)$ curve at half height (hereafter just "width.").[3,15,17] No adequate OMF K1S fits were found to be possible.

The K1 CMF model leads to the following expression

TABLE I. Fitting results for single crystal $0.88\mathrm{ZrO_2}\cdot 0.12\mathrm{Y_2O_3}$ data and various models. All fits are CNLS σ-level with PWT except for the OMF K1 ones which are NLS $M''(\omega)$ fits using UWT. Here $k=0$ for the CK0S model and 1 for the rest.

T	Model	$100\mathrm{S_F}$	β_k	$\varepsilon_{D\infty}$	A_{PC}	γ_{PC}	$\varepsilon_{Ck\infty}$	ε_∞
464 K	K1	14.2	0.423	⋯	⋯	⋯	⋯	24.6
	CK0S	0.93	0.566	⋯	⋯	⋯	0	29.9
	CK1S	0.79	0.313	22.4	⋯	⋯	5.88	28.3
	PK1	0.97	0.323	⋯	24.0	0.0045	5.50	(29.5)
503 K	K1	12.4	0.507	⋯	⋯	⋯	⋯	29.1
	CK0S	1.26	0.537	⋯	⋯	⋯	0	29.2
	CK1S	0.91	0.319	23.1	⋯	⋯	5.15	28.3
	PK1	0.55	0.322	⋯	24.2	0.0031	5.14	(29.3)
544 K	K1	4.12	0.534	⋯	⋯	⋯	⋯	29.7
	CK0S	0.84	0.512	⋯	⋯	⋯	0	30.0
	CK1S	0.87	0.319	23.9	⋯	⋯	4.75	28.7
	PK1S	0.72	0.319	⋯	25.4	0.0041	4.69	(30.1)
583 K	K1	1.53	0.571	⋯	⋯	⋯	⋯	31.2
	CK0S	0.69	0.478	⋯	⋯	⋯	0	32.4
	CK1S	0.60	0.319	25.5	⋯	⋯	4.43	29.9
	PK1S	0.58	0.318	⋯	23.6	−0.0051	4.49	(28.1)

for the high-frequency-limiting dielectric constant arising entirely from mobile charges,[12,14,15,21]

$$\begin{aligned}\varepsilon_{C1\infty} &= \sigma_0\langle\tau\rangle_{01}/\varepsilon_V\\ &= \sigma_0\tau_o\Gamma(1/\beta_1)/\beta_1\varepsilon_V\\ &= [\gamma N(qd)^2/6kT\varepsilon_V].\end{aligned}\qquad(1)$$

Here σ_0 is the dc conductivity; $\langle\tau\rangle_{01}$ is the mean of the K1 τ_o characteristic relaxation time parameter over the K0-model distribution of relaxation times, and the 01 subscript indicates that β_1, not β_0, be used in the distribution, as in the second part of the equation where $\Gamma(\,)$ is the Euler gamma function. Further, γ is defined as the fraction of charge carriers of charge q that are mobile (see later discussion); N is the maximum mobile-charge number density; and d is the rms single-hop distance for a hopping entity, sometimes written as r_{rms} or $[\langle r^2\rangle]^{1/2}$.

Note that, as shown in Eq. (1), $\varepsilon_{C1\infty}$ is a purely derived quantity, one depending only on the fitting parameters σ_0, τ_o, and β_1. For the OMF, however, $\varepsilon_{C1\infty}$ is replaced by ε_∞, a quantity that includes response associated with both mobile-charge dispersion and the dipolar-vibratory bulk-material dielectric constant $\varepsilon_{D\infty}$.[16,17] Thus, the OMF analog of Eq. (1)[17] requires that ε_∞ (or $\varepsilon_{D\infty}$) be fully determined by the purely ionic dispersion quantities σ_0, τ_o, and β_1, manifestly incorrect.[21]

The results in the table indicate that for the present data, CK0S fits are nearly as good as CK1S ones, but the former ones do not lead to separate estimates of both $\varepsilon_{D\infty}$ and $\varepsilon_{C1\infty}$. Further, for a wider frequency range, the differences in $\mathrm{S_F}$ values would be greater, making the choice of the most appropriate model much clearer. Although the proper definition of ε_∞ is $\varepsilon_\infty \equiv \varepsilon_{C1\infty}+\varepsilon_{D\infty}$, when $\gamma_{PC}\ll 1$, as it is here, A_{PC} should be a good approximation to $\varepsilon_{D\infty}$, and those quantities in the ε_∞ column of the table shown in parentheses are ε_∞ estimates based on $\varepsilon_{C1\infty}+A_{PC}$.

Because the available frequency window did not cover enough of the low-frequency response at $T=464$ K and 503 K, no significant estimates of the SCPE parameters in the PK1S model could be obtained for these temperatures. At 464 K, the peak of the $M''(\omega)$ curve was not reached, and the parameter estimates for this temperature are less well-defined than are those at higher temperatures. A similar problem for the 583 K data, but arising from insufficient high-frequency response within the available window, led to the small nonphysical[3] negative estimate of γ_{PC} shown in the table. Since its relative standard deviation was greater than 0.5, however, it cannot be well-distinguished from zero, showing that the CK1S results are more appropriate here than the PK1S ones. Nevertheless, the other very small positive values of γ_{PC}, all of which are statistically significant, indicate that NCL effects may be clearly identified in the data, although for the present data, CK1S fits yield comparable results.

It turns out that at high temperatures one sometimes finds that at the low end of the available frequency range, $\sigma'(\omega)$ response, rather than remaining constant at σ_0, slowly decreases as the frequency decreases, and $\sigma''(\omega)$ decreases to a minimum, begins to increase, may reach a peak, and finally decreases again at lower frequencies. A good example of such behavior appears in Ref. 23 for $\mathrm{CaTiO_3}$:30%Al^{3+}; it is clearly associated with electrode effects, and it may be modeled with a SCPE. Thus, such response is usually an indication of the presence of non-negligible electrode polarization contributions to the overall response, and it cannot be modeled by means of a PCPE. For the present 583 K data, the beginning of such behavior occurs at the low-frequency end of the data. Therefore, the need for a series CPE in the 544 K and 583 K fitting models indicates that electrode effects are important at these temperatures as well as are separate NCL effects.

In contrast, at sufficiently lower temperatures, both

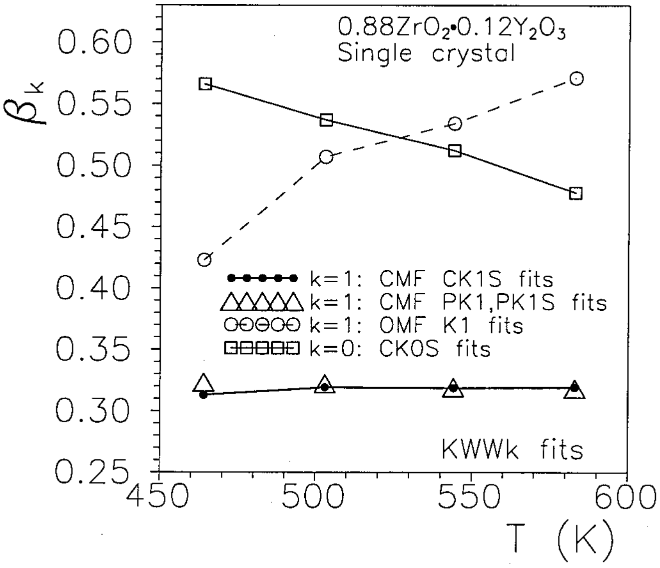

FIG. 1. β_k temperature-dependence estimates for the k and model designations listed.

$\sigma'(\omega)$ and $\sigma''(\omega)$ decrease monotonically approximately in power-law fashion, as the temperature is decreased. It turns out that they can then be fitted quite well by the addition of either a SCPE or a PCPE, for example, by CK1S or by PK1. This is evidently the case for the results for the two lower temperatures of Table I. Because the NCL behavior at these temperatures involves very small power-law exponents, there is little difference between the CK1S and PK1 models and the PK1S model is inapplicable. Thus, the results at these temperatures illustrate the fitting of NCL effects by either a series or a parallel added element.[3] Since the higher-temperature results show typical electrode-effect behavior, however, it is plausible to identify the SCPE as modeling actual electrode polarization and the PCPE as modeling NCL behavior. These identifications are confirmed by the concentration-dependence results of Sec. IV.

A. KWW shape-parameter dependencies

The various β_k $(0<\beta_k\leqslant 1)$ shape-parameter values shown in Table I are important because of their differences and because there have been many varying interpretations of them. Figure 1 shows their dependencies on temperature. Except for some uncertainty in the $T=464$ K point, we see that the CMF CK1S, PK1, and PK1S β_1 values represent the same temperature-independent behavior and lead to a K1 high-frequency-limiting power-law constant slope of $n\equiv 1-\beta_1\approx 2/3$. Although the OMF approach is incorrect, it has been so widely used that it is worthwhile to show its approximate $(\beta_1)_{\mathrm{OMF}}$ K1 response here, one which increases with increasing temperature. It shows a similar trend to earlier OMF results found in Ref. 24 for a lithium-ion conductor. Again, the corresponding limiting high-frequency power-law slope is $n_{\mathrm{OMF}}\equiv 1-(\beta_1)_{\mathrm{OMF}}$, which here decreases with increasing temperature.

The CK0S fits of the present data lead to β_0 values decreasing almost linearly with increasing temperature in the present range. Similar decreasing behavior appears for metal-nitrate mixtures in Ref. 25. Here β_0 is also the limiting high-frequency power-law exponent of the K0 response, and its interpretation when it approaches unity is somewhat anomalous.[26] Unlike the K1 model, whose intrinsic response is independent of the presence of $\varepsilon_{D\infty}$, the K0 model requires the addition to the model of a dielectric constant such as ε_∞ in order to yield a peak in the $M''_C(\omega)$ response. Thus there is no one-to-one relation between β_0 and the width, and the CK0 or CKOS model must be used for fitting in order to obtain a meaningful estimate of β_0. It follows that the magnitude of ε_∞ can influence whether the width of the $M''_C(\omega)$ curve increases or decreases as β_0 changes over a limited range. Here the dependence of β_0 on temperature leads to a decrease in the CK0 width from about 2.1 decades at 464 K to about 1.8 decades at 583 K. In most previous work, the symbol β has been used instead of β_0 or β_1, but the proper choice can usually be identified from the context.

The Ngai coupling model involves K0 response and interprets changes in β_0 with temperature as a measure of the degree to which cations interact (couple).[6,27] It follows that the approach to Debye behavior as $\beta_0\rightarrow 1$, discussed in Ref. 26, represents decreasing cation-cation interaction. The present work, however, strongly suggests that decreases in β_0 with increasing temperature arise primarily from increases of the $\varepsilon_{D\infty}/\varepsilon_{C1\infty}$ ratio in common situations where $\varepsilon_{C1\infty}$ contributes to the experimental data, as it does here. In most previous data analyses using the K0 model, no least-squares fitting of either $M(\omega)$ or $M''(\omega)$ has been carried out, and the effect of $\varepsilon_{D\infty}$ has not been separately accounted for. Thus, many if not all, previous interpretations of β_0 as a measure of correlation between mobile ions may need reconsideration.

For the present data, the CMF fits are most instructive and indicate that since β_1 remains very nearly constant, one would expect that the underlying width of the basic relaxation process would also do so. Analysis shows that the K1-only $M''_C(\omega)$ width varies only from about 3.45 decades at 464 K to about 3.40 decades at 583 K, precluding meaningful interpretation of changing ion-ion interactions in this temperature range and consistent with the lack of Coulomb interactions in the microscopic Scher–Lax response model.[20]

In summary, for the present data and probably more generally, as the temperature increases and the frequency range remains adequate $(\beta_1)_{\mathrm{OMF}}$ increases, the CMF β_1 remains virtually constant, and β_0 decreases. The low- and high-frequency slopes of the various KWWk models are discussed in detail in Ref. 26, including the use of the K0 at the ε level, the KD model. For conductive-system situations, the width of the $M''_C(\omega)$ curve at half-height increases the smaller β_1 and here at least, the larger β_0. For a pure dielectric dispersion system, it seems clear that β_D generally increases as the temperature increases, and the width of the $\varepsilon''_D(\omega)$ curve increases as β_D decreases.[28,29]

B. Further temperature dependencies

Unbiased least-squares analysis[30] of the $\tau_o(T)$ CK1S fitting results shows that this quantity may be well-described

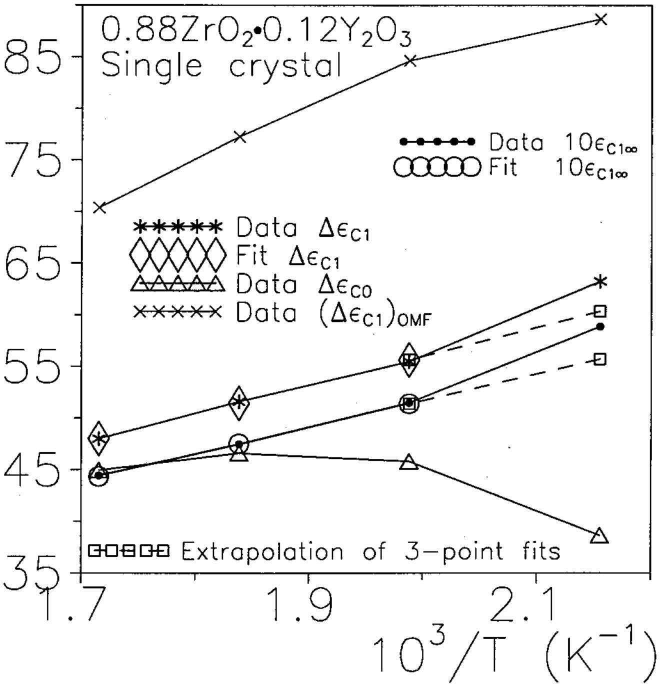

FIG. 2. Dependencies of various ε-related quantities on inverse temperature. Here $\varepsilon_{C1\infty}$ and $\Delta\varepsilon_{C1} \equiv \varepsilon_{C10} - \varepsilon_{C1\infty}$ values are derived from the CK1S-model fits, $\Delta\varepsilon_{C0} \equiv \varepsilon_{C00}$ values from CK0S fits, and $(\Delta\varepsilon_{C1})_{\mathrm{OMF}} \equiv (\varepsilon_{C10} - \varepsilon_{\infty})_{\mathrm{OMF}}$ values from K1 OMF-model fits.

by thermally activated Arrhenius behavior with an activation energy of $E_\tau = 1.218$ eV. Equation (1) leads to

$$\rho_0 = \tau_o \Gamma(1/\beta_1)/\beta_1 \varepsilon_{C1\infty} \varepsilon_V, \tag{2}$$

indicating, on using the right-hand part of Eq. (1) for $\varepsilon_{C1\infty}$, that ρ_0/T should only show Arrhenius behavior with $E_\rho = E_\tau$ when any temperature dependence of $\Gamma(1/\beta_1)/\beta_1$ is properly accounted for. Here, the CK1S estimates of β_1 are closely constant, and one obtains $E_\rho = 1.218$ eV from fitting the ρ_0/T estimates with or without the β_1 terms. On the other hand, fitting $\rho_0(T)$ estimates does not yield agreement with E_τ but leads to about a 3% smaller activation energy estimate.

The present estimate of E_ρ agrees well with the more approximate estimate of 1.22 eV presented earlier,[24] one calculated without the β_1 term. No such agreement would result from analysis of the β_1-dependent OMF K1 results using Eq. (2), with or without $\varepsilon_{C1\infty}$ replaced by ε_∞. The $\Gamma(1/\beta_1)/\beta_1$ quantity varies rapidly in the small-β_1 region, from about 9.3 at $\beta_1 = 0.3$, to 5.0 at 0.35, and to 3.3 at 0.4. The present results suggest that previous estimates of E_ρ without using the β_1 part of Eq. (2), the usual approach, should only be satisfactory for situations where the data could be adequately fit by the CMF CK1 model and no appreciable dependence of β_1 on temperature was present, as in the present work.

Figure 2 shows the dependencies of some ε-related quantities on $10^3/T$. The right-hand part of Eq. (1) indicates that $\varepsilon_{C1\infty}$ should be proportional to T^{-1}, provided the other quantities in this expression are temperature independent. Further, for the CK1S model $\Delta\varepsilon_{C1}$ is related to $\varepsilon_{C1\infty}$ by a pure function of β_1.[15] Thus, for the present situation we might expect these quantities to be proportional. For the higher three temperatures, one finds that $\varepsilon_{C1\infty} = (2.5845 \pm 0.0021)(10^3/T)$ with $\mathrm{S_F} = 0.0013$, very close indeed to T^{-1} dependence. Similarly, fitting yields $\Delta\varepsilon_{C1} = (27.984 \pm 0.050)(10^3/T)$ with $\mathrm{S_F} = 0.0031$; thus, $\Delta\varepsilon_{C1}/\varepsilon_{C1\infty} \simeq 10.83$, in full agreement with theory.[14,15] The figure shows that the points corresponding to $T = 464$ K lie above the extrapolated lines by a factor of about 1.06. This value seems unlikely to arise from the temperature dependence of the γ of Eq. (1), which should decrease from unity with increasing temperature if recombination occurs; therefore it is probably an artifact arising from the limited low-frequency data at this temperature, as already mentioned.

Recently, Sidebottom[31] proposed that the approximate expression

$$\Delta\varepsilon \equiv \varepsilon_0 - \varepsilon_\infty = \gamma N (qd)^2 / 3kT\varepsilon_V \tag{3}$$

be used as a universal scaling quantity for $\sigma'(\omega)$ data. It has been found to be useful for this purpose,[32] and this and other scaling have been recently discussed in Ref. 15. The present analysis extends these results by explaining why, and under what conditions, such scaling works and how it is related to the CMF response model.

First, note that Eq. (3) agrees with the right-hand side of Eq. (1), except for the replacement of the experimental quantity $\Delta\varepsilon$ by the theoretical one $\varepsilon_{C1\infty}$, and by the factor of 6 by 3. When a response model involving K1, such as the CK1S or PK1S, fits the data well, $\Delta\varepsilon_{C1}$ and $\Delta\varepsilon$ are essentially equal and both should show T^{-1} dependence when β_1 is temperature-independent, as discussed previously. The basic quantity is $\varepsilon_{C1\infty}$, and the present results show how it generalizes the Sidebottom expression. For the present data, using $\gamma = 1$ and the relation $d^2 = 0.35a^2$,[24] where $a = 0.516$ nm, the structural parameter of the bulk material, one finds that $N \simeq 7.65 \times 10^{20}$ cm^{-3}, probably somewhat more accurate than the value 9.0×10^{20} cm^{-3} calculated earlier for this material.[24]

Second, note that although Fig. 2 shows that $(\Delta\varepsilon_{C1})_{\mathrm{OMF}}$ can also serve approximately for scaling, $\Delta\varepsilon_{C0}$, obtained from CK0 or CK0S fitting, shows quite different behavior and would be inappropriate for this purpose. It follows that Eq. (3) should only be used for scaling for situations where a CMF dispersion model is applicable and β_1 is temperature-independent. Therefore, when such scaling is found to be appropriate, it suggests that a CMF model should be used for detailed fitting of the data.[15]

IV. CONCENTRATION DEPENDENCE

Table II shows fitting results for $x_c\mathrm{Na_2O}\cdot(1-x_c)\mathrm{GeO_2}$ frequency-response data with various sodium oxide concentrations, x_c. These data were kindly provided by Prof. D. Sidebottom; they are particularly noisy at low frequencies, so not all the low-frequency points were included in the fittings. All the fitting models used here involve K1. The first is the OMF one, as in Table II, and the others are versions of the CMF approach, all involving CNLS fitting of the full $\sigma(\omega)$ data.

Although the CK1S estimates of $\varepsilon_{D\infty}$ and the PK1 estimates of $A_{PC} \simeq \varepsilon_{D\infty}$ are somewhat uncertain, rough extrapo-

TABLE II. Fitting results for $x_c\mathrm{Na_2O}\cdot(1-x_c)\mathrm{GeO_2}$ data with different x_c values and various models. All fits shown involved PWT.

x_c/T	Model	$100S_F$	β_1	$\varepsilon_{D\infty}$, $\varepsilon_{D\infty0}$	A_{PC}	γ_{PC}	$\varepsilon_{C1\infty}$	ε_∞
0.003	K1	13.5	0.611	⋯	⋯	⋯	⋯	5.48
308 K	CK1	3.23	0.333	5.63	⋯	⋯	0.411	6.04
	CK1S	2.92	0.357	5.54	⋯	⋯	0.483	6.02
	PK1	3.25	0.351	⋯	5.63	0.00089	0.455	(6.09)
	$\mathrm{C_{fi}PK1}$	3.10	0.342	5.0	0.648	0.0078	0.423	(6.07)
0.01	K1	12.1	0.523	⋯	⋯	⋯	⋯	6.56
284 K	CK1	4.60	0.368	5.51	⋯	⋯	1.47	6.98
	CK1S	2.44	0.356	5.89	⋯	⋯	1.18	7.07
	PK1	3.48	0.354	⋯	6.04	0.0019	1.17	(7.27)
	$\mathrm{C_{fi}PK1}$	3.47	0.352	5.0	1.09	0.0126	1.14	(7.23)
0.03	K1	11.1	0.439	⋯	⋯	⋯	⋯	7.01
278 K	CK1	5.50	0.340	4.95	⋯	⋯	2.42	7.37
	CK1S	1.76	0.348	5.03	⋯	⋯	2.48	7.51
	PK1	1.30	0.349	⋯	5.69	0.0063	2.35	(8.04)
	$\mathrm{C_{fi}PK1}$	1.64	0.344	5.0	1.65	0.0920	2.16	(7.81)
0.1	K1	12.9	0.426	⋯	⋯	⋯	⋯	9.98
263 K	CK1	6.27	0.348	7.81	⋯	⋯	4.29	12.1
	CK1S	2.92	0.360	6.62	⋯	⋯	4.26	10.9
	PK1	1.23	0.364	⋯	7.85	0.0095	4.08	(11.9)
	$\mathrm{C_{fi}PK1}$	1.42	0.348	5.0	3.53	0.0260	3.48	(12.0)

lation of their values to $x_c=0$ suggests that a common value for $\varepsilon_{D\infty0}$ of 5.0 is reasonable. This value has been used in the $\mathrm{C_{Fi}PK1}$ model, where the $\varepsilon_{D\infty}$ parameter has been taken fixed at $\varepsilon_{D\infty0}$. Note that the PK1 model, through its PCPE part, requires one to assume that there is dielectric dispersion of the full $\varepsilon_D(\omega)$ response, contrary to the usual assumption that any dispersion associated only with the bulk material occurs at frequencies much beyond the highest in the present data. The $\mathrm{C_{Fi}PK1}$ model involves the more plausible assumption that $\varepsilon_D(\omega)$ is undispersed over the experimental range in the absence of any ionic effects, and, when charge-carrier effects are present, the induced bulk dielectric dispersion is associated only with a PK1 model where $(A_{PC})_{\mathrm{C_{fi}PK1}} \simeq [(A_{PC})_{\mathrm{PK1}}-\varepsilon_{D\infty0}] \approx (\varepsilon_{D\infty}-\varepsilon_{D\infty0})$, appropriate when $\gamma_{PC} \ll 1$. Since this inequality is reasonably well-satisfied by the present results, we shall set $(A_{PC})_{\mathrm{C_{fi}PK1}}=\Delta\varepsilon_{D\infty}$. Note that the present results deal only with NCL in conductive systems and suggest that NCL disappears at zero ionic concentration. Nevertheless, it appears that a different type of NCL may also appear in insulators.[5,33]

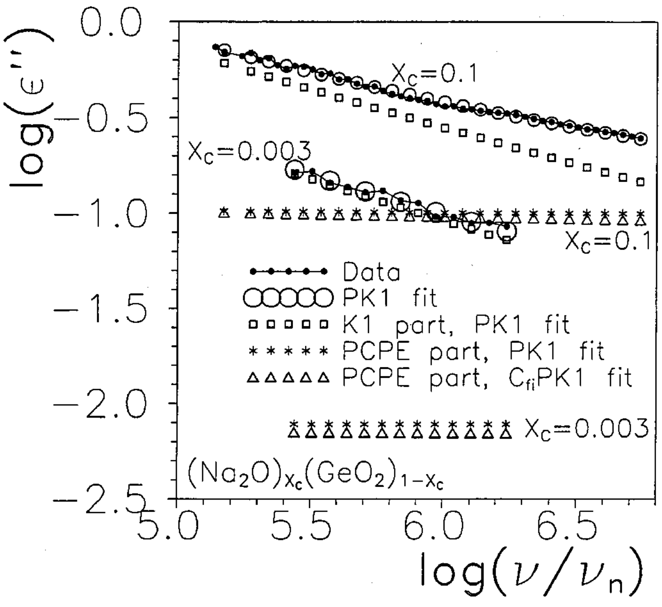

FIG. 3. Log–log plots of $\varepsilon''(\nu)$ data and fits vs frequency, ν, for two relative ion concentrations, x_c. Also shown are the estimates associated with the separate K1 and PCPE parts of the composite fitting models. Here $\nu_n=1$ Hz.

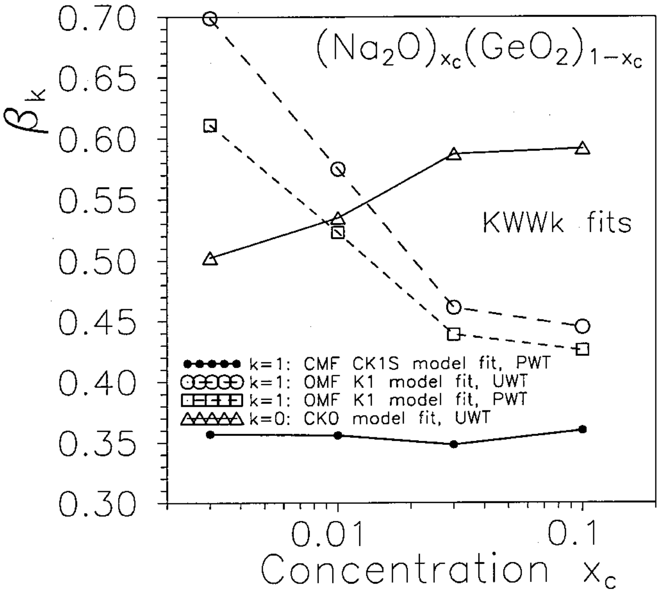

FIG. 4. β_k concentration-dependence estimates for fits with various models. Here PWT and UWT indicate proportional and unity weighting, respectively.

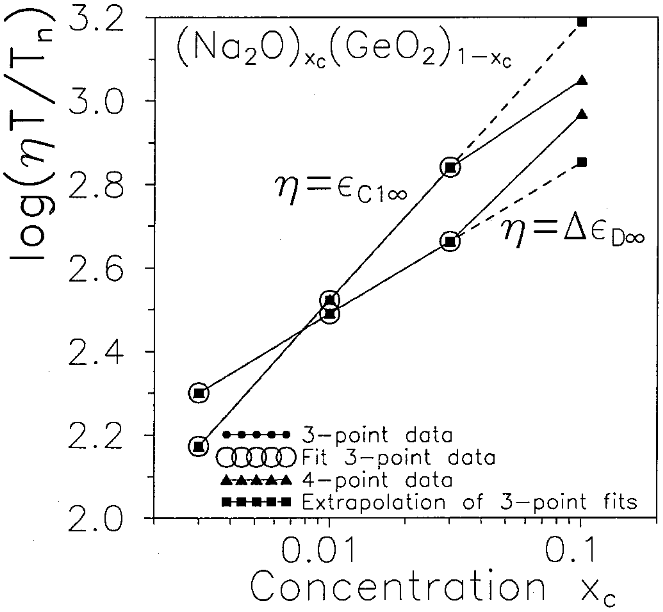

FIG. 5. Log–log plots of ηT for designated η quantities. Here $\Delta\varepsilon_{D\infty}$ is the A_{PC} quantity listed in Table II and involves the fixed value $\varepsilon_{D\infty 0}=5.0$, and $T_n=1$ K.

Figure 3 presents fitting results for the two extreme values of x_c. Although the fits involved the full data (minus some extreme outlying points) extending from about 4 Hz to 5×10^6 Hz, only results for the highest-frequency points are included here for increased resolution. Table II shows that even though the tabular values of γ_{PC} associated with PK1 and C_{Fi}PK1 differ appreciably, their nearly-constant-loss PCPE contributions to the fit in the figure are quite close to each other, in agreement with the rough equality of the S_F values for the two full-fitting models. The figure also shows those parts of the fit arising only from the K1 part of the model: lines with slopes of $-\beta_1$ which are not a part of the NCL response.

Figure 4 shows the dependencies of the various β_k quantities on concentration. We see that, except for a small deviation of the $x_c=0.1$ point, the CK1S β_1 values are closely independent of ion concentration. Although the OMF K1 results shown in Table II involve PWT, the figure compares both PWT and UWT OMF estimates. The UWT results lead to better estimates of the widths of the experimental $M''(\omega)$ curves, ones that always include $\varepsilon_{D\infty}$ effects, and so are not representative of the true CMF K1-model $M''_C(\omega)$ widths.[3,15]

The UWT OMF results are qualitatively similar to OMF ones obtained by Patel and Martin and others on various alkali glasses.[34–37] The results included in Ref. 35 for the same material as that considered here are mostly comparable to the present ones, making it clear that their $\beta=1-n$ results are actually OMF β_1 ones rather than K0 β_0 ones. These same results are included in Ref. 38 where, however, they are misidentified as stretched-exponential Kohlrausch exponents β (i.e., β_0). Figure 4 shows that β_0 increases, rather than decreases, as the concentration increases, opposite behavior to that of the OMF β_1 parameter. Since, unlike the CMF, the OMF approach yields β_1 estimates that do not represent the actual β_1 values appropriate for the K1 model alone, all such OMF estimates are, however, nugatory and should not be used to assess ion–ion correlation effects.

Figure 5 shows some interesting and significant results. In the past I have stated that $\varepsilon_{D\infty}$ and the dielectric effects associated only with mobile charges should be independent to first order.[15] The figure shows, however, that since both the bulk dielectric increment $\Delta\varepsilon_{D\infty}$ and $\varepsilon_{C1\infty}$ depend strongly on x_c, $\varepsilon_{D\infty}$ and $\varepsilon_{C1\infty}$ are mutually dependent, indicating appreciable coupling between ionic and bulk processes, the origin of NCL behavior of the present kind.

The three lowest points of each line in Fig. 5 are exceptionally well-fitted by an equation of the form

$$T\eta=B_\infty\Lambda x_c^m. \tag{4}$$

For the $\eta=\varepsilon_{C1\infty}$ choice with $\Lambda=\gamma$ fixed at unity, one finds $B_\infty=7166\pm 19$, $m=2/3$, and $S_F=0.0046$. Equation (4) is consistent with the right-hand side of Eq. (1), provided one sets $N\propto x_c$ and $\gamma d^2\propto x_c^{-1/3}$. For the $\eta=\Delta\varepsilon_{D\infty}$ situation, a fit with Eq. (4) and $\Lambda=1$ leads to $B_\infty=1631\pm 14$, $m=0.362\pm 0.002$, and $S_F=0.0031$. Now it turns out that here estimates of m are appreciably dependent on the value of $\varepsilon_{D\infty 0}$, and a choice of 4.975 rather than 5 leads to a slightly better fit than that listed and to $m=0.335\pm 0.002$. It thus appears that $m=1/3$ is an appropriate value for this situation.

How can we explain these exponent values? If the mobile ions were homogeneously distributed and fully dissociated, one would expect that the interionic separation distance, $d_{\mathrm{Na-Na}}$, should be proportional to $x_c^{-1/3}$, consistent with the transport-distance dependence for small x_c obtained in Refs. 39 and 40 for the present material but inconsistent with the present $\varepsilon_{C1\infty}$ dependence, one where the d of Eq. (1) is closely proportional to $x_c^{-1/6}$. There is, at present, no good explanation for this discrepancy but it suggests that the d of Eq. (1) may not be the same quantity as $d_{\mathrm{Na-Na}}$ in the small-x_c region. It is worth noting that although Sidebottom,[31] on analyzing the present data with Eq. (3), stated that his γd^2 results were roughly proportional to $x_c^{-2/3}$, in fact his three smallest-x_c points are much more consistent with the accurate $x_c^{-1/3}$ dependence found here.

The present $T\Delta\varepsilon_{D\infty}\propto x_c^{1/3}$ result also requires explanation. First, consider the differences between the extrapolated lines and the actual $x_c=0.1$ points shown in Fig. 5. For the $\varepsilon_{C1\infty}$ situation, a value of $\Lambda=\gamma\simeq 0.73$ at this concentration yields agreement with the data. We can now rule out the possibility that $\Delta\varepsilon_{D\infty}$ is proportional to $(\varepsilon_{C1\infty})^{1/2}$, even though this choice yields exponent agreement. The figure shows that in order to change the extrapolated $\Delta\varepsilon_{D\infty}$ point so that it agrees with the data, one would require a value of $\Lambda=\gamma$ greater than unity on using this square-root relation. Instead, if we posit that for this situation $\Lambda=1/\gamma$ and assume that $\Delta\varepsilon_{D\infty}$ is proportional to $1/\gamma d^2$, along with the present $\varepsilon_{C1\infty}$ result that $d^2\propto x_c^{-1/3}$, then a value of $\gamma\simeq 0.76$ leads to agreement. The two values of γ are sufficiently close to each other that the present $\varepsilon_{C1\infty}$, and $\Delta\varepsilon_{D\infty}$ relations may be taken as consistent.

We may interpret the above $\gamma<1$ results in several ways. Although unlikely, they may arise only from a Haven ratio less than unity at this higher concentration.[39] More likely is that there is some ion association at this concentration. The present results lead to quantitative dependencies of the interesting NCL-related quantity $\Delta\varepsilon_{D\infty}$ on temperature and on $1/\gamma d^2$, but not directly on N.

V. DISCUSSION

Future analysis should try to explain the present NCL behavior in terms of a microscopic model that shows how high-frequency vibrational motion of ions can augment the high-frequency polarization of the bulk material, thus leading to NCL of the type identified herein. The present identification of NCL as a bulk dielectric phenomenon does not ascribe observed NCL behavior directly to localized ionic vibration as in Refs. 4 and 5 but invokes coupling of such motion to the surrounding nonionic elements of the material. The present results suggest that a small part of the energy of vibrating ions is transferred to the bulk material, resulting in increased bulk polarization at high frequencies and thus to an increase in $\varepsilon_{D\infty}$ dependent on the mean separation of the ions. It seems likely that such a theory would need to involve both electromagnetic interactions between ions and surrounding bulk dipoles, as well as contributions from high-frequency phonons.

Development of a theory to explain the present temperature- and concentration-dependence results should wait for the resolution of an outstanding problem discussed following. The excellent frequency-response data fits herein strongly suggest that the data include simultaneous contributions from ionic dispersion (the K1 term in the fitting model), dielectric NCL (the P or PCPE term), and electrode effects (the S or SCPE) term. Note that all these elements contribute to the total response at all frequencies, although with variable weight as the frequency changes. It follows that the present NCL coupling process is operative at all frequencies, as well as just causing the high-frequency-limiting dielectric quantity $\varepsilon_{D\infty}$ to increase with increasing ionic concentration. These results are consistent with both appreciable temperature and ionic-concentration variation. In contrast, the outstanding and significant work of Ref. 4 seems, however, to lead to different conclusions about the origin of NCL in ionically conducting materials.

In Ref. 4, León *et al.* propose ‘‘a serial picture in which NCL ceases to exist when ions leave their cages and start hopping.’’ They thus conclude that NCL contributions do not exist at the lowest frequencies and that therefore one cannot describe the full response by two mechanisms in parallel. Acceptance of this conclusion would rule out the applicability of the PK1 (or C_{Fi}PK1) model of the present work. León *et al.*[4] authors base most of their conclusions on their demonstration of a crossover in $\sigma'(\omega)$ data at constant frequency and variable temperature between a NCL process at sufficiently low temperatures and/or high frequencies to power-law ion hopping at high temperatures and/or low frequencies. Further, they find that the crossover frequency is thermally activated with a low-activation energy identified with the barrier that ions must overcome to begin hopping.

First, it should be noted that no CNLS fitting has been carried out for the work described in Ref. 4, and no mention is made there of possible electrode effects. But such effects may be important at either low or high frequency ends of the frequency range.[3,12,13,15,23] Thus, they may possibly be mistaken for NCL in some ranges where the data may be fitted with either a SCPE or PCPE added element, and where bulk dispersive response, such as that associated here with K1, may be of minor or no importance.

Here, where good fitting often requires both a PCPE and an SCPE in the model, it is evident that the PCPE term leads to dielectric NCL behavior and the SCPE one accounts for electrode effects. When this is the case, the serial approach of Ref. 4 would seem to be inapplicable unless the high-temperature parts of the response were ascribed to electrode effects. Then, the present parallel dielectric model for NCL may still be consistent with some or all of the Ref. 4 data and results. It remains to be shown, however, whether either the parallel PK1 or the series CK1S model can lead to the transitional effect demonstrated in Ref. 4 and as well, to results showing low-temperature NCL behavior, such as those presented in Figs. 7 and 9 of Ref. 41. Work in progress is aimed at evaluating these possibilities, and preliminary results seem promising for both models.

ACKNOWLEDGMENT

It is a pleasure to thank Dr. Carlos León for stimulating, valuable, and often contrarian discussions relevant to the area of the present work.

[1] B. S. Lim, A. V. Vaysleyb, and A. S. Nowick, Appl. Phys. A: Solids Surf. **56**, 8 (1993).
[2] A. S. Nowick, A. V. Vaysleyb, H. Jain, and X. Lu, Mater. Res. Soc. Symp. Proc. **411**, 99 (1996).
[3] J. R. Macdonald, J. Chem. Phys. **115**, 6192 (2001); J. Non-Cryst. Solids (to be published).
[4] C. León, A. Rivera, A. Várez, J. Sanz, J. Santamaria, and K. L. Ngai, Phys. Rev. Lett. **86**, 1279 (2001); A. Rivera, C. León, J. Sanz, J. Santamaria, C. T. Moynihan, and K. L. Ngai, Phys. Rev. B (submitted).
[5] K. L. Ngai, J. Chem. Phys. **110**, 10576 (1999).
[6] K. L. Ngai and A. K. Rizos, Phys. Rev. Lett. **76**, 1296 (1996).
[7] J. R. Macdonald, J. Appl. Phys. **84**, 812 (1998).
[8] K. Funke and D. Wilmer, Solid State Ionics **136–137**, 1329 (2000).
[9] J. R. Macdonald, Solid State Ionics **124**, 1 (1999). Erratum: the heading ‘‘Appendix’’ is missing and should appear following the third line of the Acknowledgments Section, p. 10.
[10] J. R. Macdonald and L. D. Potter, Jr., Solid State Ionics **23**, 61 (1987); J. R. Macdonald, J. Comput. Phys. **157**, 280 (2000). The newest version of the comprehensive LEVM fitting program may be downloaded at no cost from http://www.physics.unc.edu/~macd/. It includes an extensive manual, executable programs, and full source code. More information is provided about LEVM at this www address.
[11] R. Kohlrausch, Pogg. Ann. der Phys. und Chemie (2) **91**, 179 (1854); G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).
[12] J. R. Macdonald, J. Non-Cryst. Solids **212**, 95 (1997). Erratum: *ibid.* **220**, 107 (1997). In addition, the symbol σ should be removed from the right end of Eq. (12).
[13] J. R. Macdonald, Solid State Ionics **133**, 79 (2000).
[14] J. R. Macdonald, Phys. Rev. B **63**, 052205 (2001).
[15] J. R. Macdonald, J. Appl. Phys. **90**, 153 (2001). In Eq. (10), $\sigma_0\Gamma$ should be replaced by $\sigma_0\tau_o\Gamma$.
[16] P. B. Macedo, C. T. Moynihan, and R. Bose, Phys. Chem. Glasses **13**, 171 (1972).
[17] C. T. Moynihan, L. P. Boesch, and N. L. Laberge, Phys. Chem. Glasses **14**, 122 (1973).
[18] K. L. Ngai and C. León, Phys. Rev. B **60**, 9396 (1999).
[19] J. R. Macdonald, J. Non-Cryst. Solids **197**, 83 (1996). Erratum: *ibid.* **204**, 309 (1996). In addition, G_D in Eq. (A2) should be G_{CD}.
[20] H. Scher and M. Lax, Phys. Rev. B **7**, 4491 (1973).
[21] J. R. Macdonald, Solid State Ionics (submitted).

[22] A. Pimenov, J. Ullrich, P. Lunkenheimer, A. Loidl, and C. H. Ruscher, Solid State Ionics **109**, 111 (1998).
[23] J. R. Macdonald, J. Non-Cryst. Solids **210**, 70 (1997).
[24] C. León, M. L. Lucia, J. Santamaria, M. A. Paris, J. Sanz, and A. Várez, Phys. Rev. B **54**, 184 (1996).
[25] A. Pimenov, P. Lunkenheimer, M. Nicklas, R. Böhmer, A. Loidl, and C. A. Angell, J. Non-Cryst. Solids **220**, 93 (1997).
[26] J. R. Macdonald, J. Appl. Phys. **82**, 3962 (1997).
[27] K. L. Ngai and S. W. Martin, Phys. Rev. B **40**, 10550 (1989).
[28] N. O. Birge, Y. H. Jeong, S. R. Nagel, S. Bhattacharya, and S. Susman, Phys. Rev. B **30**, 2306 (1984).
[29] X. Xia and P. G. Wolynes, Phys. Rev. Lett. **86**, 5526 (2001).
[30] J. R. Macdonald and W. J. Thompson, Am. J. Phys. **59**, 854 (1991).
[31] D. L. Sidebottom, Phys. Rev. Lett. **82**, 2653 (1999).
[32] J. C. Dyre and T. B. Schrøder, Rev. Mod. Phys. **72**, 873 (2000).
[33] A. K. Jonscher, IEEE Trans. Dielectr. Electr. Insul. **8**, 345 (2001).
[34] S. W. Martin and C. A. Angell, J. Non-Cryst. Solids **83**, 185 (1986).
[35] K. L. Ngai, J. N. Mundy, H. Jain, O. Kanert, and G. Balzer-Jollenbeck, Phys. Rev. B **39**, 6169 (1989).
[36] H. K. Patel and S. W. Martin, Phys. Rev. B **45**, 10292 (1992).
[37] A. Pan and A. Ghosh, Phys. Rev. B **59**, 899 (1999).
[38] K. L. Ngai and S. W. Martin, Phys. Rev. B **40**, 10550 (1989).
[39] D. L. Sidebottom, P. F. Green, and R. K. Brow, J. Non-Cryst. Solids **222**, 354 (1997).
[40] B. Roling, C. Martiny, and K. Funke, J. Non-Cryst. Solids **249**, 201 (1999).
[41] A. S. Nowick, A. V. Vaysleyb, and W. Liu, Solid State Ionics **105**, 121 (1998).