"Constant-loss" relaxation response in crystals and glasses

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Abstract. Nowick and his associates have stated that many ionic crystals and glasses exhibit a loss per cycle which is independent of frequency over an appreciable range and have suggested that such behavior constitutes a "new universality". Furthermore, much such data seem to approach an asymptotic, nearly temperature-independent ac loss at sufficiently low temperatures. In order to further evaluate these conclusions, small-signal ac relaxation data for a $CaTiO_3 : 30\% \, Al^{3+}$ ceramic material are analyzed in detail and the results compared to those published by Nowick and associates for the same material. It is found that a plausible conducting-system dispersion model based on the effective-medium approximation for hopping charges yields results globally similar to, but somewhat different in detail from, those of Nowick et al. But a response model which includes both such conducting-system response and dielectric-system dispersion well fits the data over a wide temperature range. To do so, it requires the presence of a non-zero high-frequency-limiting resistivity probably arising from localized charge motion. No constant-loss individual dispersions appear in the model, but it nevertheless yields approximately constant loss over a limited frequency range at low temperatures. It suggests that asymptotic behavior is associated with the nearly temperature-independent dielectric-dispersion contribution to the response at low temperatures, and it does not verify the Nowick conclusion that the slope of the ac conductivity approaches a constant value near 0.6 at high temperatures.

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In a recent article on the present subject, Lim, Vaysleyb, and Nowick [1] (abbreviated hereafter as LVN) discussed their and earlier [2, 3] observations "that, at low temperatures, the ac conductivity $\sigma(\omega)$ is proportional to frequency ω, corresponding to a loss per cycle that is independent of frequency" [1]. These authors [1–3] have suggested that because of the appearance of such behavior for a wide range of materials it constitutes a "new universality", a very important conclusion if it is indeed justified. Further, in their interesting work, LVN concluded that such "constant-loss" behavior is a bulk property of the material but not one which is thermally activated. In their work, they did not provide a model describing in detail their combined temperature and frequency response observations and stated that "constant-loss behavior needs to be further studied in order to better show which factors control this behavior and thereby to point the way to a more suitable model to describe it". In the present work, I provide a plausible explanation for such apparent constant-loss response.

The complex conductivity is given by $\sigma(\omega) \equiv \sigma'(\omega) + i\sigma''(\omega)$, and the full complex dielectric constant by $\varepsilon(\omega) \equiv \varepsilon'(\omega) - i\varepsilon''(\omega)$, where $\varepsilon(\omega) = \sigma(\omega)/(i\omega\varepsilon_V)$ and ε_V is the permittivity of vacuum. Now it is important to note that plotting of data in log-log form, especially with a wide scale so that resolution is low, can obscure a multiplicity of irregularities [4, 5]. Such plotting of $\log[\sigma'(\omega)]$ or $\log[\varepsilon''(\omega)]$ versus $\log(\omega)$ is extremely common in the present field, although, alternatively, linear plots of the real and imaginary parts of the complex modulus, $M(\omega) \equiv [\varepsilon(\omega)]^{-1}$, provide much higher resolution, especially at higher frequencies [6, 7].

It is thus legitimate to ask whether one can indeed properly conclude from such log-log plots that $s(\omega) = 1$ over several decades of frequency [1–3] and, if such constant-loss exists, whether it is even associated with conductive-system response. The log-log slope $s(\omega)$ is associated with response of the form $[\sigma'(\omega) - \sigma'(0)] \propto \omega^{s(\omega)}$. In most of the previous work in the present area, $s(\omega)$ is taken as a constant rather than as a frequency-dependent quantity [1–3], certainly not always a good approximation even over a limited frequency range [6]. Because of the relationship between σ' and ε'', a value of s for conductivity data leads to a slope of $(1 - s)$ for the corresponding log-log ε'' data from which the effects of $\sigma'(0)$ have been removed.

The conclusion of a recent detailed analysis of relaxation data on single-crystal NaCl kindly provided to me by Nowick stated [6]: "In view of the present results, it seems possible that there is no new universality for the

other conducting crystals, glasses, and disordered solids measured by Nowick, his associates, and other workers; that appropriate and detailed analysis of more accurate data would show that the slope values involved in such conductive-system dispersion are nearly always less than unity; and that $s(\omega)$ never equals unity over an appreciable frequency range unless it is associated with pure dielectric dispersion or possibly with a combination of that and conductive-system dispersion." In contrast, Lee et al. [2] found that $s = 1$ over a wide temperature range for NaCl. But Nowick has recently stated [8]: "We conclude that the behavior of the highly disordered materials is totally different from that of NaCl". Clearly, differences of opinion exist for this area, ones which I address herein. Although Funke [9] has written "the difficulty is removed by the observation that a genuine $s = 1$ power law of the conductivity does not exist", the present analysis suggests that the matter is probably somewhat more complicated.

A particularly interesting feature of the LVN data and of considerable earlier relaxation data for highly disordered solids is the appearance of an apparent minimum or floor in the $\varepsilon''(\omega)$ response as the temperature decreases to low values (or, equivalently, the approach of $\sigma'(\omega)$ curves toward a minimum asymptotic curve, often one with $s(\omega)$ apparently close to or equal to unity). Below a particular temperature, further temperature reductions reduce $\varepsilon''(\omega)$ only marginally, although the actual apparent limiting value seems to depend on the particular material measured [1]. But Huang and Johari [10] dispute, on the basis of measurements on a SiO_2 glass down to 163 K, that a limiting frequency- and temperature-independent value of ε'' is indeed approached at low temperatures. Although LVN cite the work of Burns et al. [11] as showing that it is even possible to obtain $s = 1$ behavior in glasses at extremely high frequencies and room temperature, these authors and Cole and Tombari [12], who discuss the Burns work, make no such claim but instead only mention that there are indications of an approach to $s = 1$ at high frequencies (see the discussion below of this possibility).

Further, it should be noted that Conductive-System Dispersion (CSD), that is usually associated with non-localized hopping charge carriers which can percolate through the entire material, undergoes a transition to localized two-level tunneling behavior at sufficiently low temperatures [13]. Finally, it is not always recognized that CSD leads to increments in both the real and imaginary parts of the full complex dielectric constant [6, 7]. Thus, in situations where both CSD and Dielectric-System Dispersion (DSD) are simultaneously present in the same frequency range [14, 15], it must be expected that $\varepsilon''(\omega)$ involves contributions from both sources, as does $\sigma'(\omega)$. In the present work, I investigate this possibility for essentially the same data as that discussed by LVN.

1 Data

In their work [1], since LVN present more relaxation data for $CaTiO_3$ doped with 30% Al^{3+} than for other materials, it seems appropriate to consider these results here. In 1992 Nowick was kind enough to send me data on this material, which are used herein for fitting. These data involve a
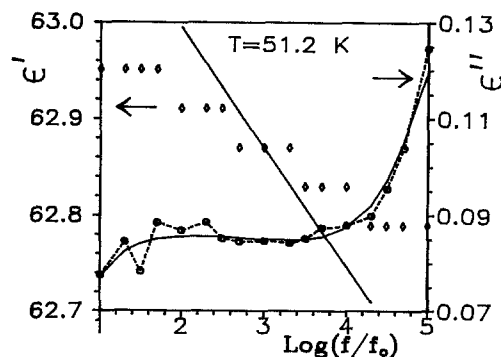

Fig. 1. Complex-dielectric-constant relaxation response of $CaTiO_3$ doped with 30% Al^{3+} at $T = 51.2$ K (*points* and *dashed line*). The two *solid lines* are CNLS fit results using the Conductive-Dielectric system (C-D) model discussed in the text. Here, $f_0 = 1$ Hz

different cell constant than that published in [1], and most of the temperatures of measurement are somewhat different, but the general behavior seems closely consistent, and where the temperature is the same (e.g., 531 K), detailed agreement with the data of [1] is found. We shall particularly concentrate on the available data sets for the lowest temperatures ($T = 51.2$ K to 212.7 K) because LVN have identified the range of 64 K to 224 K as that of constant loss for this material.

But there are some problems with both the data considered here and those of [1], all measured with the same techniques. First, the data have low resolution, with only four points per frequency decade, although a minimum of 10 is desirable. Second, the data are irregular, apparently containing appreciable errors. Finally, the relatively narrow range of frequencies covered, $f = 1$ Hz to 10^5 Hz, limits full appreciation of the behavior of the material. Some of these problems are illustrated in Fig. 1, plotted with a linear rather than logarithmic scale. Complex Non-linear Least Squares (CNLS) fits of the data to a model discussed subsequently are shown as solid lines and were carried out using the readily available LEVM V.6.1 CNLS fitting program [16, 17]. This procedure, which involves fitting real and imaginary data components simultaneously, has been employed for all of the fits of the present work. It ensures that all fit results obey the Kronig-Kramers transform relations [6, 18]. Proportional weighting or function power-law weighting [16, 17] was used for all fits here.

In Fig. 1, the poor resolution of the ε data, particularly that of ε', is particularly evident. The solid-line fit result for ε' deviates somewhat from the corresponding data points, but note the extremely small range of variation shown here. Such deviation does not appear for data at 393 K and above. Although Fig. 1 does show a limited ε'' region of nearly zero slope, the total variation for the frequency range shown is over 50%, certainly hard to reconcile with $s = 1$ behavior over an appreciable range.

2 Conductive-system response

Since $CaTiO_3 : Al^{3+}$ is an oxygen-ion conductor, it is reasonable to ask whether its frequency/temperature re-

sponse can be entirely described by a CSD response model, one involving a frequency-independent dielectric constant associated with non-dispersive behavior of the lattice dipoles of the material, $\Delta\varepsilon_D'$, over the range of frequencies measured. Although they do not discuss the matter fully, this also appears to be the assumption made by LVN. In the following, the letter "D" will be used to denote quantities associated with DSD response, "C" to denote those associated with a conducting system, and, where necessary, "C-D" to designate combined response.

Two recent extensive reviews [19, 20] deal with detailed CSD models, as does a review of the Funke jump-relaxation model [9], one which involves correlated hopping. Of particular interest is the effective medium approach [4, 20], since Dyre [21] has suggested that it leads to a universal response function in the limit of low temperatures. But the result, an equation originally derived by Bryksin [22], appears only in normalized form in this limit and so is not useful in its original form for direct comparison with unnormalized data.

Because of this limitation, I have recently extended the approach to non-zero temperatures [7], building on earlier work of Dyre [4, 21]. An approximate equation derived from this approach, which will be designated here as the BDM equation, is discussed in the Appendix. It depends on temperature only through the normalized activation energy quantity x_c and has been incorporated in the LEVM fitting program, V.6.1, so that it may be readily used for data fitting. A crucial strength of the BDM equation is that it well predicts [7] the excess high-frequency-tail absorption generally seen at the complex modulus, M'', level and characterized by Moynihan et al. [23] as "endemic in the solid state". It also yields Davidson-Cole-like dispersion when the dc conductivity is subtracted out and the results are transformed to the complex dielectric constant level and plotted in the complex plane, but again very-slow-decay excess loss appears at the highest frequencies [7].

Interestingly, the BDM leads to complex-plane impedance curves that are remarkably close to those of Funke [9]. But a particular virtue of the BDM is that it requires many fewer parameters for its full expression for any appropriate frequency and temperature than does the much more complex Funke relaxation expression. The BDM requires only two parameter values, while even the many empirical relaxation response functions used in the past (Cole-Cole, Davidson-Cole, Kohlrausch-Williams-Watts, etc.) each require a minimum of four for thermally activated response. For these reasons, and because it may, in fact, possibly be of nearly universal applicability for hopping situations, the BDM is exclusively used herein to fit the conducting-system part of the measured response.

We begin by considering CSD response alone (no dielectric dispersion). LVN have presented a graph of log(σ') versus log(f) data containing curves for 15 different temperatures. In Fig. 2, a similar set of conductive-system $\sigma' \equiv \sigma'_C$ curves are presented which were calculated using the BDM equation. The temperature value for each curve is listed in the figure caption and is identified by the same letter used by LVN in their work. Therefore, the present curves may be directly compared with those of the same temperature in Fig. 1 of [1]. There is a slight ambiguity,
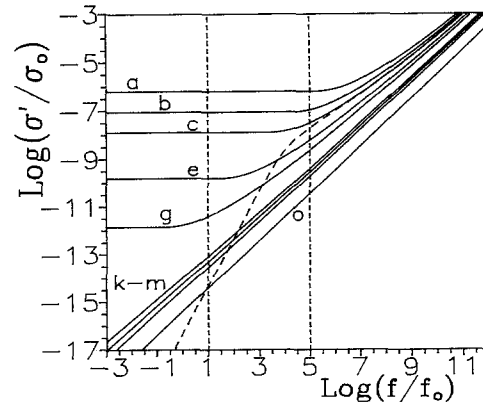

Fig. 2. Variation of theoretical conductive-system conductivity, $\sigma'(\omega)$, with frequency for temperatures (a) 625 K, (b) 574 K, (c) 531 K, (e) 454 K, (g) 393 K, (k) 244K, (l) 211 K, (m) 174 K, and (o) 55K. The curves were calculated with the BDM equation using only the dc resistivity, $\rho'(0) \equiv \sigma'(0)^{-1}$, and the activation energy estimated from the LVN data for $CaTiO_3 : 30\%$ Al^{3+} [1]. The temperatures correspond to those with the same letters in the LVN work. The dashed curve, for 531 K, is that for $\sigma'(\omega) - \sigma'(0)$, and the normalizing quantity $\sigma_o = 1$ $(\Omega cm)^{-1}$. The vertical dashed lines define the LVN data window

however, because LVN actually identify temperatures for only 14 of their 15 curves. The missing temperature is actually 144 K [8].

The frequency window of the LVN data is shown by the vertical dotted lines in Fig. 2, but the frequency range is much extended here in order to show more details of the conductive response. The dashed line, for $T = 531$ K (curve c), is that for $\sigma(\omega) - \sigma(0)$ and shows the proper limiting low-frequency slope of 2. The BDM curves were calculated for given frequency and temperature values with only two inputs: the activation energy of $\sigma'(0)$, E_c, and its infinite-temperature limiting value, σ_{aC}, expressed in terms of the limiting-barrier attempt time or hopping time, τ_{aC} (see (A-1) in the Appendix). Thus, the full temperature and frequency response of the conducting system is completely defined by the two parameters describing the thermally activated expression for the dc conductivity or resistivity; no other fitting parameters were used or needed. For all of the present work, the actual values $E_c = 1.19$ eV and $\tau_{aC} = 1.73 \times 10^{-17}$ s were used. They were estimated from least-squares Arrhenius fitting of the temperature dependence of the LVN $\sigma'(0)$ data as read off their Fig. 1. The normalized effective-medium frequency, $\Omega_E \equiv \omega\tau_C$, defined in the Appendix, becomes exceedingly large at low temperatures because τ_C is thermally activated. For example, for the present input values one finds $\tau_C \simeq 2.2 \times 10^{-7}$ s at $T = 625$ K and about 8×10^{93} s at $T = 55$ K.

Comparison of the curves of the present Fig. 2 with the corresponding ones in the LVN work show that the general behavior is extremely similar, with the higher-temperature, lower-frequency values agreeing fairly closely with the LVN results (except for a separate drop-off at low frequencies and high temperatures in the LVN data ascribed by them to electrode blocking effects). But especially note that the CSD results show much less of an approach to an asymptotic limiting curve for σ' at the lowest temperatures than does the LVN data. Further, the BDM equation leads to frequency-dependent high-frequency slopes [7, 21, 22], unlike the empirical relations mentioned above
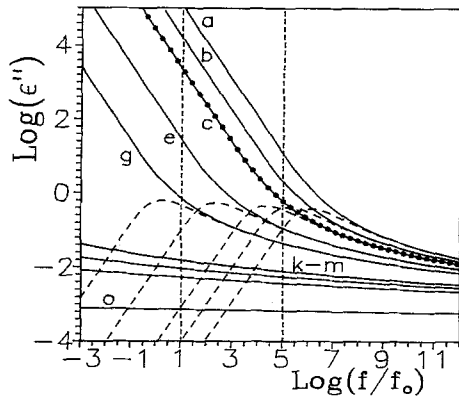
Fig. 3. Log-log theoretical $\varepsilon''(\omega) \equiv \Delta\varepsilon_C''$ conductive-system response curves calculated directly from the BDM curves of Fig. 2 with the same identification letters. The *circles* are predictions obtained by accurate solution of the basic effective-medium equation (see Appendix). The *dashed* $\Delta_G\varepsilon_C''$ lines were calculated from $\sigma'(\omega) - \sigma'(0)$ rather than $\sigma'(\omega)$, and so they represent the dielectric-loss response of a conductive system with the dc conductivity removed

Fig. 4. Temperature dependences of the real- and imaginary-part conductive-system dielectric increments for fixed frequencies of 0, 10^{-5}, and 10^3 Hz. The top x_c scale corresponds to the temperature scale at the bottom for the present choice of $E_c = 1.19$ eV

where the limiting slopes are frequency independent. For very large Ω_E values, the log-log σ' slope, $s \equiv s'$, approaches $1 - [\ln(\Omega_E)]^{-1}$. The actual slope predicted by the BDM equation at $T = 50$ K is about 0.992 over the LVN frequency window, a value which would be very hard to distinguish from unity.

By plotting the ε'' results corresponding to those for σ' in Fig. 2, one reduces the range of variation of the data appreciably, obtains greater resolution, and allows the possibility of constant-loss behavior to be more directly evaluated. Figure 3 shows such results. Here $\varepsilon'' \equiv \varepsilon_C'' \equiv \Delta\varepsilon_C''$. The solid points included on curve c were obtained directly from an accurate solution for the roots of the effective-medium implicit equation for $x_c = 26.006$, the value of this normalized quantity at $T = 531$ K for $E_c = 1.19$ eV. Their close agreement with the approximate BDM predictions for this temperature verifies the accuracy of the latter equation, one which becomes more and more accurate as the temperature decreases.

The agreement within the LVN window of the present ε'' results with the corresponding LVN curves is similar to that for Fig. 2, but now we can see that even at the higher temperatures, where agreement is close at 10 Hz, the ε_C'' values lie appreciably below the data values at 10^5 Hz. Further, although the conductive-system BDM equation indeed leads to very nearly constant loss at low temperatures (e.g., curve o for 55 K), no real floor is predicted. In fact, it can be shown that in the limit of large Ω, $\varepsilon_C'' \rightarrow (\pi/2)/\ln^2(\Omega_E)$. For sufficiently low temperatures, this expression leads to $\varepsilon_C'' \propto T^2$.

Also shown in Fig. 3 are five curves of $\Delta_G\varepsilon_C'' \equiv [\sigma'(\omega) - \sigma'(0)]/i\omega\varepsilon_V$. For curves k–o, such subtraction led to negligible effects since the peaks at these low temperatures occur for frequencies much less than 10^{-3} Hz. The peak frequencies here are thermally activated with $\omega_p\tau_p = 1$ and τ_p proportional to τ_C. Further, the peak heights are closely proportional to $\Delta\varepsilon_C'(0)$ and thus decrease somewhat faster than proportional to T^{-1} in this range, as illustrated in Fig. 4. In this figure, which shows some x_c values along the top, the temperature dependences for
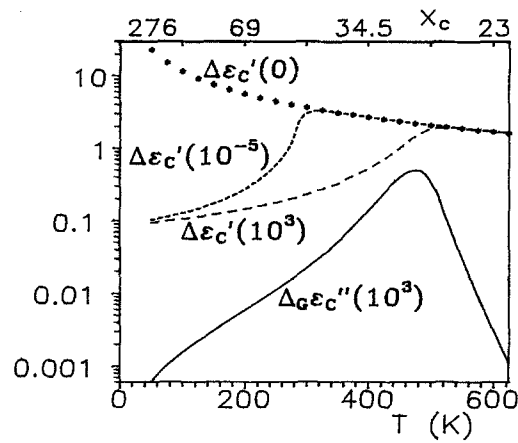
$\Delta_G\varepsilon_C''$ and $\Delta\varepsilon_C'$ are shown for several fixed frequencies. The results for $\Delta\varepsilon_C'(0)$ depend only on x_c, but the others also depend on τ_{aC}. For high temperatures such as 531 K, $\Delta_G\varepsilon_C''(1000)$ is proportional to τ_{aC} over a wide range, but, at much lower temperatures, dependence is greatly reduced. For example, at 200 K when τ_{aC} is reduced (increased) by a factor of ten from its present value, $\Delta_G\varepsilon_C''(1000)$ increases (decreases) by only 13% (12%), showing $1/\ln^2(\tau_{aC})$ dependence, in close agreement with the limiting logarithmic behavior cited above.

If one accepts that the BDM equation is universal for conductive-system response, or even approximately so, comparison of the present results with the data of LVN shows that much of the theoretical response lies somewhat below the corresponding data curves. Thus it seems most likely that conductive-system response alone cannot explain the data, and that therefore one needs to invoke simultaneous dielectric-system dispersion as well. This possibility is investigated below.

3 Combined dispersive response

When both conductive- and dielectric-system effects are present in the same frequency range, one can write the following expression for the combined response [6, 15],

$$\sigma(\omega) \equiv \sigma_C(\omega) + \sigma_D(\omega) = [\rho_C'(\infty) + \Delta\rho_C'I_C(\omega)]^{-1}$$
$$+ i\omega\varepsilon_V[\varepsilon_D(\infty) + \Delta\varepsilon_D'I_D(\omega)], \quad (1)$$

where $\Delta\rho_C' \equiv \rho_C'(0) - \rho_C'(\infty)$ and $\Delta\varepsilon_D' \equiv \varepsilon_D'(0) - \varepsilon_D'(\infty)$. The $I(\omega)$ functions describe the dispersions and satisfy $I(0) = 1$ and $I(\infty) = 0$. For I_C, I shall continue to use the BDM equation and, for reasons which will soon be apparent, I shall use the Exponential Distribution of Activation Energies [EDAE] equation for I_D. Both functions are discussed in the Appendix and are available as fitting models in LEVM.

The solid lines in Fig. 1 for the $T = 51.2$ K data were obtained by CNLS fitting to such a C-D model, one that required a non-zero value of $\rho_C'(\infty)$ to obtain an adequate fit at the high-frequency end of the data set. It is of particu-
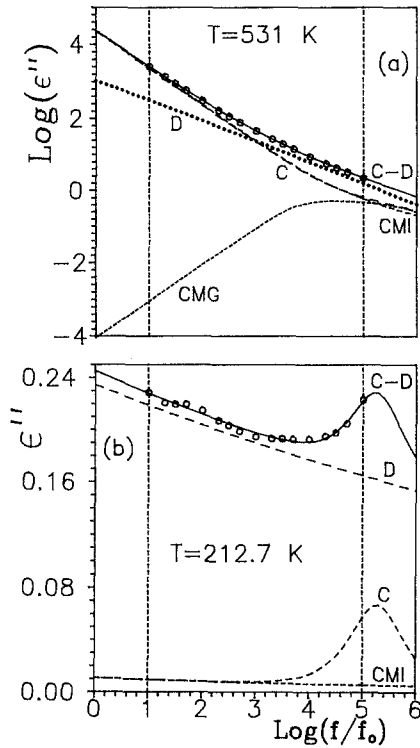
Fig. 5a, b. Dissection showing the various contributions to the C-D model ε'' fit results for relatively low- and relatively high-temperature data (*circular points*). *Solid lines* show the C-D fits; D and C identify the separate dielectric and conductive contributions; the CMI line is that for the conductive-system with the effects of the high-frequency-limiting resistivity, $\rho_C'(\infty)$, removed; and the CMG curve of a is the same as the C line but with the effect of $\sigma'(0)$ removed. For 212.7 K, the difference between C and CMG curves is negligible. The fit results have been extrapolated a decade on either side of the data window
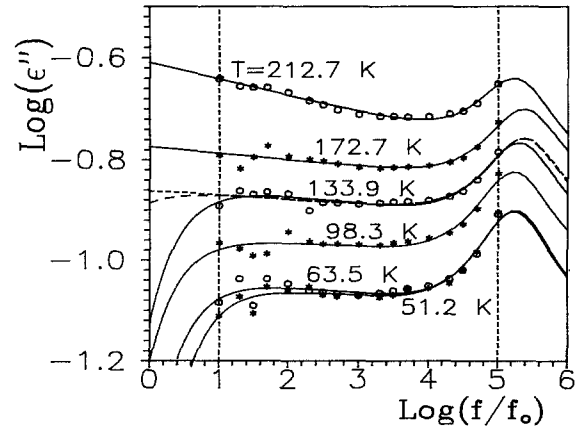

Fig. 6. Results of CNLS fitting of the C-D model to six low-temperature $\varepsilon''(\omega)$ data sets. The fit results have been extrapolated a decade on either side of the data window

lar interest to see how the various terms in (1) individually contribute to the overall fit of $\varepsilon''(\omega)$. Such dissection of the response is illustrated in Fig. 5 for relatively low and relatively high temperatures; here the fitting results have been extrapolated one decade on either side of the LVN data window. The various curves are identified in the figure caption. Fig. 5a, which has had to be plotted on a logarithmic scale to illustrate pertinent details, shows that $\Delta\varepsilon_C''$ (curve C) dominates at the lower frequencies where the effects of $\sigma'(0)$ are still important, while $\Delta\varepsilon_D''$ does so at the higher ones. The parameter ϕ_D of the EDAE model was estimated to be about 0.60 here, yielding -0.60 for the estimated log-log slope of $\Delta\varepsilon_D''$ (curve D) [15, 24]. It is clear that, since the C and CMI curves are nearly identical up to 10^5 Hz, $\rho_C'(\infty)$ only begins to be important at higher frequencies for this temperature, and it was, in fact, only estimated from the data with large relative uncertainty.

The situation is appreciably different for the results shown in Fig. 5b, plotted on a linear scale. Here subtraction of $\sigma'(0)$ makes no difference, and we see that although $\Delta\varepsilon_C''$ still plays a small role, the response is dominated by $\Delta\varepsilon_D''$ except at the high frequency end where the $\rho_C'(\infty)$ contribution to $\Delta\varepsilon_C''$ becomes dominant. As expected, it is much better determined here and is found to be of the order of 7×10^7 Ωcm. By contrast, at this temperature $\Delta\rho_C' \simeq 6.1 \times 10^{24}$ Ωcm. Because $\tau_C \simeq 2.8 \times 10^{12}$ s, however, the term $\Delta\rho_C'I_C(\omega)]$ in (1) is very much smaller than

$\Delta\rho_C'$. Here the slope estimate, $-\phi_D$, is about -0.03, small but certainly not zero, and the τ_D estimate is about 400 s.

As the results of Fig. 5b show, the peaked response occurring between $f = 10^5$ Hz and 10^6 Hz is an intrinsic feature of the BDM conductive-system response. It has been found that if ω_P is the angular frequency of the peak, then $\Delta\varepsilon_C''(\omega_P) \simeq \Delta\varepsilon_C'(\omega_P)$ and $2\omega_P\varepsilon_V\Delta\varepsilon_C'(\omega_P)\rho_C'(\infty) \simeq 1$, indicating that for sufficiently small $\rho_C'(\infty)$, no such peaked response will occur within the measurement range.

Figure 6 shows fitting results for the six lower-temperature data sets, plotted on an expanded log scale. We see that the data and fit results are very nearly the same for the two lowest temperatures, probably defining the limiting ε'' floor. The fit estimates of $\rho_C'(\infty)$ were constant at about 10^8 Ωcm within their estimated standard deviations for the three lowest temperatures and appear to decrease slowly for the higher temperatures. The data are inadequate to determine whether $\rho_C'(\infty)$ and/or τ_D are thermally activated or not. In the present temperature range, $\Delta\varepsilon_D'$ increases approximately linearly with temperature for $T \geq 63.5$ K. For dielectric dispersion, the EDAE model predicts that ϕ_D may be directly proportional to temperature [15, 24]. Because of the limitations of the data already mentioned, only a general trend, roughly consistent with such behavior, is observed.

The limited accuracy and range of the data leads to very high correlations in the fit results between the fitting parameters $\Delta\varepsilon_D'$, τ_D, and ϕ_D, particularly at the higher temperatures of Fig. 6. The resulting very shallow minimum in τ_D makes its estimate uncertain. The problem is illustrated by the three $T = 133.9$ K curves of the figure. The solid one is that obtained with all five dielectric dispersion parameters free, leading to the rather poorly defined estimate $\tau_D \simeq 0.168$ s. The two curves lying above it were obtained with τ_D fixed at 1.68 s and 16.8 s, respectively. Although these changes affect the low-frequency end of the curve appreciably, the relative standard deviations of the fits for the three cases [16, 17] were 0.0146, 0.0158; and 0.0161, for increasing τ_D values, showing almost insignificant increases. Further, it is obvious from the figure that a relatively small increase in the value of the lowest-frequency data point would have led to an appreciably
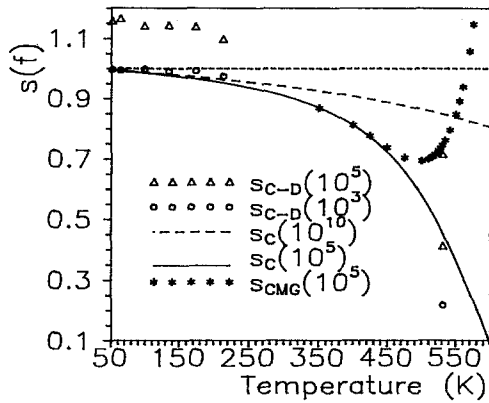
Fig. 7. Temperature dependences of the log-log slopes, $s(f)$, for C-D fits and BDM-equation conductive-system predictions for frequencies of 10^3, 10^5, and 10^{10} Hz. The slopes were calculated with the dc conductivity, $\sigma'(0)$, subtracted from $\sigma'(\omega)$ except for the *solid-line* curves and except for the two $T = 531$ K *triangular* and *circular points* with values less than 0.5. The horizontal *dashed line* is drawn at $s = 1$

larger estimate of τ_D than 0.168 s. In spite of these parameter-estimation difficulties, Fig. 6 shows that the present approach allows the data to be fit very well, a result not possible over the temperature range of the LVN data with either CSD or DSD alone.

Figure 7 shows slope values at various fixed frequencies for some of the different fitting possibilities. All slope results shown are with the effect of $\sigma'(0)$ removed, except those for the solid line and the two $T = 531$ K triangular and circular points with values less than 0.5. The C-D results were obtained by quintic-spline fitting of the fit curves, not the data themselves [6, 25], and the others from such fitting of BDM results. We see that at 10^3 Hz, the low-temperature C-D slopes are very close to unity but slightly below it, while at 10^5 Hz they are near 1.1 because of the influence of $\rho_C'(\infty)$. All three of the CSD s_C curves were calculated with $\rho_C'(\infty) = 0$.

The $s_{CMG}(10^5)$ curve defined by the asterisk points shows the slope of $\sigma'(\omega) - \sigma'(0)$ rather than that for $\sigma'(\omega)$, as in the solid-line curve. Comparison of the two $f = 10^5$ CSD curves shows the large effect of accurate subtraction at high temperatures. The high-temperature rise of the s_{CMG} curve is caused by the progressive approach towards the limiting slope value of 2 shown, for example, in the dashed curve of Fig. 2. The upper triangular point at 531 K shows that the slope at 10^5 Hz is nearly the same for the combined C-D response as it is for the CSD response alone. The corresponding C-D slope at $f = 10^3$ Hz, 1.9, is off the top of the graph. The unsubtracted C-D slope at the same frequency, the bottom circular point, is about 0.22, very different indeed.

LVN presented a slope curve for $CaTiO_3 : Al^{3+}$ (their Fig. 3) that is similar in shape to the solid line in Fig. 7 except in two respects: first, some low-temperature values exceed unity, and second, their curve approaches a constant value of about 0.5 at 531 K and above.

To account for their results, LVN proposed a fitting equation of the form

$$\sigma'(\omega) = \sigma'(0) + A_0\omega^s + A_1\omega^{1.0}, \tag{2}$$

where $s \sim 0.6$, A_0 is thermally activated, A_1 is not, and the last term accounts for constant-loss behavior [1]. As a test of the appropriateness of this equation, which ignores $\sigma''(\omega)$ response, for the present material I fit it, using nonlinear least squares, to $T = 625.7$ K data, data which agree well with the 625 K curves presented by LVN. A fairly good fit was obtained, although the actual $\sigma'(\omega)$ data values are clearly not well described by two power-law responses in parallel. The fit was slightly better with A_1 non-zero, but the relative standard deviation of A_1 was nearly 10, showing that the data allowed no sensible estimate of this quantity. Further, $\sigma'(0)$ was not well defined, and the s estimates were about 0.2 (0.16) with $A_1 = 0$ and 0.22 (0.45) with A_1 non-zero, both values very different from 0.5. Here quantities such as 0.16 and 0.45 are the relative standard deviations of the parameter estimates.

Comparison of the results of this fitting, and that of the present C-D approach, with the Fig. 7 results for $T = 531$ K, certainly indicates no approach to the temperature-independent value of s near 0.5 to 0.6 found by Nowick and his associates [1–3]. But examination of the s_{CMG} curve of Fig. 7 suggests that their approximately constant slope estimates over an appreciable high temperature range may possibly have arisen from subtraction of inaccurate values of $\sigma'(0)$ in forming $\sigma'(\omega) - \sigma'(0)$ at each temperature.

For the present material, no comparisons of results with different cell thickness have been published [1]. Such results would be useful in allowing one to distinguish between thickness-independent electrode effects and thickness-dependent bulk response and might possibly allow one to ascribe the $s \approx 0.2$ value mentioned above to a series electrode-response contribution.

The present results suggest that a C-D model, such as that used herein, is appropriate for describing and understanding data of the present kind. It explains a possible low-temperature asymptotic limiting response for σ' and ε'', such as those apparent in the present data, as arising from dominant nearly-temperature-independent dielectric dispersion at low temperatures, requires a non-zero value of $\rho_C'(\infty)$ for good fitting of the data, and does not justify the $s = 1$ "new universality" proposed by Nowick and his associates [1, 2]. Just as no new universality was found to be justified from the NaCl analysis [6] and a non-zero value of $\rho_C'(\infty)$ was required there as well, it seems plausible that a C-D approach such as that employed here can adequately explain most of the dispersive response found for disordered crystals and glasses without the assumption of a true constant-loss frequency response region of significant extent.

Appendix

In this appendix the BDM conductive-system response equation and the dielectric-system EDAE equation are briefly discussed. Consider a thermally activated situation where a relaxation time, τ, is given by

$$\tau = \tau_{aj}\exp(E/k_B T), \tag{A1}$$

where $j = $ C or D. Here τ_{aj}^{-1} is a barrier attempt frequency

(usually 10^{12} Hz or greater), and the activation energy E satisfies $0 \leq E \leq E_H$.

A1 BDM equation

The derivation of this equation for a hopping situation has been discussed earlier [7]. One starts by averaging an effective-medium equation for the conductivity over a random free-energy barrier probability distribution which is zero outside the E range defined above (a box distribution) [4]. The resulting equation for the conductivity, termed the GBEM equation in [7], involves $E_c \equiv E_H/3$ and τ_{aC} and leads to a saturation value of σ_C' at very high frequencies and to a corresponding decrease in σ_C'' [7]. All the temperature dependence of the equation arises from that of the normalized maximum effective-activation energy, $x_c \equiv E_c/k_B T$. The crossover frequency, f_{co}, that where $\sigma_C' = \sigma_C''$, occurs at $f_{co} \simeq 0.22 \, (x_c \tau_{aC})^{-1}$. For the present data, f_{co} is greater than 5×10^{14} Hz, and thus this part of the response may be neglected here.

There may be a contribution to $\rho_C'(\infty)$ both from percolating charges [7], say $\rho_{CP}'(\infty)$ and from local-neighborhood charge motions which do not involve percolation throughout the entire material [6], $\rho_{CNP}'(\infty)$. Since it turns out that $\rho_{CP}'(\infty)$ is virtually always negligible compared to $\rho_C'(\omega)$, it can be neglected, and we shall take $\rho_C'(\infty) = \rho_{CNP}'(\infty)$. Now define the strength of the percolation contribution to the dispersion as $\Delta\rho_C'$. Then $\rho_C(\omega) = \rho_C'(\infty) + \Delta\rho_C' I_C(\omega)$. The $T \to 0$ limit of the GBEM equation is the solution of the following implicit complex equation (the Bryksin equation [22]) for I_C,

$$\ln I_C = -i\Omega_E I_C, \tag{A2}$$

where $\Omega_E \equiv \omega\tau_C$ is a normalized frequency variable. Here, $\tau_C \equiv \Delta\rho_C' \varepsilon_V \varepsilon_C'(0)$. Temperature-dependent expressions for $\Delta\rho_C'$ and $\varepsilon_C'(0)$ follow from the GBEM treatment [7]. They are

$$\Delta\rho_C' = (\tau_{aC}/\varepsilon_V)R_x \tag{A3}$$

and

$$\varepsilon_C'(0) \simeq 0.0853 T_x x_c . \tag{A4}$$

Here,

$$R_x \equiv 2\exp(x_c)/[1 + \exp(-x_c)] , \tag{A5}$$

and T_x is a temperature-dependent quantity closely approximated by $1 - 1.5 \, x_c^{-1}$ for the x_c range from ∞ to 20 and approaching $x_c/4$ as $x_c \to 0$. Instead of using the fit parameters E_c and τ_{aC}, one can alternatively use $\Delta\rho_C'$ and τ_C, although their high correlation makes this a less appropriate choice. The GBEM-equation prediction, $\rho_{CP}'(\infty)$, is $(\tau_{aC}/\varepsilon_V)$, many orders of magnitude smaller than the $\rho_{CNP}'(\infty)$ quantity found from fitting the present data.

Although GBEM values of σ_N are the solution of a much more complicated implicit equation than (A2), it has been found [7] that for $f \ll f_{co}$, its unnormalized results are close to those of (A2) when (A4) and (A5) are used. In order to obtain a data-fitting equation which does not require the solution of an implicit equation for every frequency value, accurate $\sigma_N(\Omega_E)$ results calculated using (A2) have been fit with LEVM to an interpolating expression,

the BDM equation. Its error in fitting both the $T \to 0$ limit of the GBEM and its $T > 0$ predictions is small compared to typical experimental errors provided that $f \ll f_{co}$. The BDM, which involves many fixed fitting parameters, and an expression for T_x for all temperatures, have been incorporated as a unified distributed circuit element in LEVM V. 6.1. Thus, conductive-system relaxation data can now be readily fit using the BDM equation.

A2 The EDAE equation

The normalized I_D dielectric response function which appears in (1) may be expressed as [15, 24]

$$I_D(\Omega_H) \equiv \phi_D[1 - \exp(-\phi x_s)]^{-1} \int_0^{x_H} \frac{\exp(-\phi_D x)\,dx}{1 + i\Omega_H \exp(-x)}, \tag{A6}$$

where $x_H \equiv E_H/k_B T$; $\Omega_H \equiv \omega\tau_D$; and $\tau_D \equiv \tau_{aD}\exp(x_H)$. Here ϕ_D is a parameter different from, but related to, the slope of the log-log frequency response. For the flat-top-box probability distribution, $\phi_D = 0$, and for this and some other values of ϕ_D closed form expressions are available for I_D [24]. It has been incorporated into LEVM as a distributed circuit element, so the EDAE model can be used to fit data for any value of ϕ_D.

As discussed elsewhere, ϕ_D may be either temperature independent or dependent [15, 24]. In the latter case, its simplest temperature dependence is direct proportionality to the absolute temperature. Then $\phi_D = 0$ can only occur at absolute zero, but this limitation does not apply when it is temperature independent. This value of ϕ_D leads to $s = 1$ at the conductivity level. None of the usual empirical relaxation functions, such as that of Havriliak and Negami [26], can yield such a result. Finally, note that for ϕ_D appreciably less than unity and $\Omega_H \gg 1$, the log-log slopes of $\varepsilon_D' - \varepsilon_D'(\infty)$ and ε_D'' are approximately $-\phi_D$, and the larger is ϕ_D the narrower the dispersion response [5, 15]. The quantity x_H also limits the width of the response, and it is often difficult to determine from data of limited frequency range. For the present work, it has been taken large enough to avoid any such limitation.

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