

# ac complex conductivity in NaCl: No new universality

J. Ross Macdonald

Department of Physics and Astronomy, University of North Carolina, Chapel Hill,  
North Carolina 27599-3255

(Received 24 March 1993; accepted for publication 4 October 1993)

A new universality has been recently proposed by Lee, Liu, and Nowick [Phys. Rev. Lett. **67**, 1559 (1991)] for dispersion in high-resistivity crystalline and disordered solids which posits that the real part of the conductivity  $\sigma'$  exhibits  $\omega^\gamma$  frequency response, with  $\gamma=1$  over an appreciable temperature range. To investigate this surprising conclusion in further detail, several powerful analysis methods were applied to Lee and co-worker's ac relaxation data for single-crystal NaCl doped with  $\text{Zn}^{2+}$ . In the past, no significant information has been obtained from the  $\sigma''$  data. Complex nonlinear least-squares fitting was used to analyze simultaneously both parts of the admittance data,  $Y(\omega) = Y'(\omega) + iY''(\omega)$ , with several conductive-system response models. The dispersive part of the response is here generally very small compared to the low-frequency-limiting conductance,  $G_0$  and capacitance. New forms of the Barton, Nakajima, and Namikawa relation were derived and shown to be applicable for the data and the most appropriate model. Contrary to previous work, analysis and interpretation in terms of conductive-system dispersion, rather than dielectric dispersion, led to new results which vitiate the new universality assumption. Arrhenius plotting of  $G_0(T)$  yielded a curved line, but a split of  $R_0 \equiv G_0^{-1} \equiv R_\infty + \Delta R$ , into the undispersed high-frequency-limiting part  $R_\infty$  and the strength of the dispersed part  $\Delta R$ , showed that while both quantities were separately thermally activated,  $R_\infty$  exhibited a large, abrupt entropy transition near 363 K. From these results the vacancy migration activation energy was estimated to be 0.695 eV, and the  $R_\infty$  vacancy-association activation energy changed from about 0.66 eV below the transition to about 0.56 above it, suggesting a transition from nearest-neighbor association to next-nearest-neighbor association.

## I. INTRODUCTION AND BACKGROUND

This work is concerned with finding a universe in a grain of sand. The grain of sand is the small-signal frequency response data of Lee, Liu, and Nowick<sup>1</sup> (abbreviated below as LLN) for single-crystal NaCl doped with divalent Zn at 50 ppm and fitted with gold-paint electrodes. There are eight data sets covering the temperature range from 23 to 260 °C, each with 17 frequencies extending from 10 to 10<sup>5</sup> Hz. The data were provided in the form of conductance  $G$  and capacitance  $C$  values, and in the present work they were first transformed to the admittance level,

$$Y(\omega) \equiv Y'(\omega) + iY''(\omega) = G(\omega) + i\omega C(\omega).$$

The  $Y'(\omega)$  results are shown on the log-log plot of Fig. 1 and appear to be of classical form.

LLN characterized their data in terms of three principal attributes: a power-law exponent of unity for the frequency response of  $Y'$  at the five lower temperatures; "essentially" frequency-independent capacitance; and an Arrhenius activation energy of the dc conductivity of 0.95 eV. These attributes are sufficient to define an approximate averaged response for the material but leave unexamined its far more interesting detailed universe of response explored in part herein. The original NaCl data were said to involve uncertainties of the order of 1%, and temperature was stated<sup>2</sup> to be controlled to within 1 °C; but, note that a 1 K change in absolute temperature near 296 K leads to about a 14% change in a thermally activated quantity having an activation energy of 1 eV.

Based on the above results and on frequency-response data for other materials, LLN proposed a "new universality" in the ac conductivity of ionically conducting crystals and glasses.<sup>1</sup> It is concerned with the behavior of the exponent  $\gamma$  in the common expression for the frequency response of the real part of the conductivity,

$$\sigma(\omega) \equiv \sigma'(\omega) + i\sigma''(\omega) \equiv (l/A)Y(\omega),$$

namely<sup>1</sup>

$$\sigma'(\omega) = \sigma_0 + a\omega^\gamma, \quad (1)$$

where the empty-cell capacitance is  $C_c \equiv \epsilon_V(A/l)$ ;  $\epsilon_V$  is the vacuum permittivity;  $\sigma_0 \equiv \sigma'(0) \equiv (l/A)G_0$  is the dc conductivity; and  $a$  is a possibly temperature-dependent parameter. The proposed universality is that, within the frequency range where power-law response is present,  $\gamma=1$  at relatively low temperatures and that this is a universal phenomenon for such materials.

Note especially, however, that LLN  $\gamma$  values were determined from the slope of a log-log graph of  $Y'(\omega)$  versus frequency at frequencies where  $Y'(\omega) \gg G_0$ , appropriate if the slope is indeed constant with frequency.<sup>1</sup> Alternatively, values of  $\gamma$  are also often estimated from least-squares fitting of equations such as Eq. (1), but both techniques yield averaged values when  $\gamma$  actually varies with frequency (i.e., approximate but not exact power-law behavior is present). Although LLN have followed past practice and designated the present  $\gamma$  by the letter  $s$ , suggesting that  $\gamma$  is indeed the frequency-independent slope of a log-log curve,  $s$  will be reserved here for the actual frequency-dependent

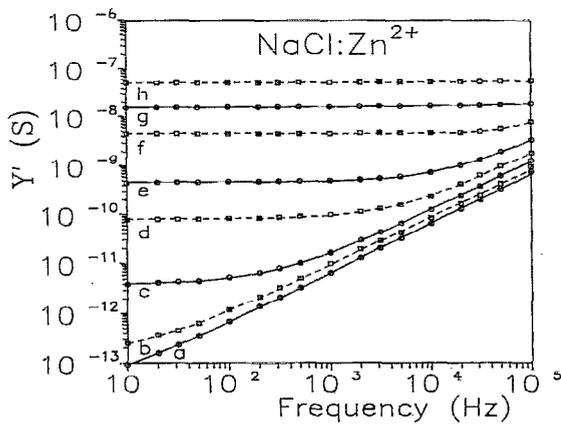


FIG. 1. Variation of conductance  $Y'(\omega)$ , with frequency for eight temperatures. The points shown on the curves are for (a) 296.2; (b) 328.7; (c) 363.2; (d) 400.7; (e) 429.2; (f) 470.7; (g) 499.7; and (h) 553.2 K. The solid lines are nonlinear-least-squares-fitting results.

log-log slope of a  $[\sigma'(\omega) - \sigma_0]$  conductivity<sup>3,4</sup> or  $\Delta_G Y'(\omega) \equiv [Y'(\omega) - G_0]$  conductance curve, quantities not calculated by LLN,<sup>1</sup> Lee *et al.*,<sup>3</sup> and Lim and co-workers<sup>4</sup> but examined in detail herein. For simplicity hereafter, "slope" will be taken to mean slope of a log-log curve.

Because of the importance of the LLN new universality, if it is indeed found to be a general phenomenon, it seemed appropriate to use some new and powerful methods to reanalyze some of the data leading to this conclusion. On request, LLN kindly sent me their data, and the present work discusses the results of some further analysis of their simplest, but most surprising, findings, those obtained for doped NaCl. For this material, LLN found that  $\gamma = 1$  over the temperature range from 298 to 475 K, while for some other materials<sup>1,3,4</sup> they observed that  $\gamma$  reached unity only at temperatures below 200 K, decreased at higher temperatures, and finally approached a constant value of 0.6 for  $T > 300$  K.

Although there have been other  $\gamma \approx 1$  results reported in the literature<sup>5-8</sup> before the work of LLN, there have been little or none that show unequivocally that  $\gamma$  remains at unity over appreciable frequency and temperature ranges. Funke<sup>8</sup> has even suggested that a genuine  $\gamma = 1$  conductivity power law does not exist, and as we shall see, there are serious difficulties with the concept when it is taken to mean that  $s(\omega) = 1$  from some given frequency up to indefinitely large frequencies.

Since  $\gamma$  is an averaged quantity when it is obtained from data fitting, for any claim that  $\gamma = 1$  one should specify the range of frequencies over which fitting yielded an estimate of  $\gamma = 1$  and, most important, whether  $s(\omega)$ , the actual slope of a log-log plot of the ac conductance data, was also constant in the range and equal to unity within experimental error. If it was not, a  $\gamma = 1$  estimate is of little significance since it might arise from values of  $s(\omega)$  which increased systematically from below 1 to above 1. Only if  $s(\omega)$  is found to vary around unity with random errors (no systematic behavior) is it appropriate to claim on the basis

of a fit-estimate value of  $\gamma = 1$  that the situation involves constant energy loss at the dielectric level, as Lim, Vaynslyb, and Nowick (LVN)<sup>4</sup> have recently done.

Conventionally, one obtains complex dielectric constant response from the total admittance of the system as

$$\epsilon(\omega) \equiv e'(\omega) - ie''(\omega) \equiv Y(\omega)/(i\omega C_c).$$

It will include effects arising from dielectric and conductive-system dispersion if both processes are simultaneously active. At low frequencies the response becomes dominated by  $G_0$  and  $C_0$ , where  $C_0 \equiv C_c \epsilon'(0)$  is the low-frequency-limiting value of the parallel capacitance of the system. Here, however, this bulk capacitance is not of primary interest because, as we shall see, there is no significant dielectric dispersion present in the NaCl data. Instead, we will be concerned with conducting-system dispersion and with the dielectric increment  $\Delta_c \epsilon$  arising from such dispersion. In order to calculate the real and imaginary parts of this increment, one must form the quantities

$$\begin{aligned} \Delta_{CG} Y(\omega) &\equiv Y(\omega) - i\omega C_0 - G_0 \\ &\equiv \Delta_C Y(\omega) - G_0 \\ &\equiv \Delta_G Y(\omega) - i\omega C_0 \end{aligned} \quad (2)$$

and

$$\Delta_c \epsilon(\omega) \equiv \Delta_c \epsilon'(\omega) - i\Delta_c \epsilon''(\omega) \equiv \Delta_{CG} Y(\omega)/(i\omega C_c). \quad (3)$$

Both the real and imaginary part subtractions may involve small differences between nearly equal large numbers when  $|\Delta_c \epsilon(\omega)| \ll |\epsilon(\omega)|$ , as is the case for the present data. These subtractions lead to relative-error magnification; thus,  $C_0$  and  $G_0$  should be determined as accurately as possible when such subtractions are necessary.

The ac energy loss arising from conductive-system dispersion is proportional to  $\Delta_c \epsilon'' \equiv \Delta_G Y''/(\omega C_c)$  and will indeed be frequency independent if  $\Delta_G Y'$  is proportional to  $\omega$  (then ideally,  $\gamma = s = 1$ ). Because it is easier to recognize systematic deviations from data with a constant slope of zero than from data with a slope of unity, when constant energy loss is suspected it is most appropriate to plot  $\Delta_c \epsilon''(\omega)$  vs  $\omega$  (or vs  $\Delta_c \epsilon'$ —a Cole-Cole plot<sup>9</sup>) rather than  $\Delta_G Y'(\omega)$ . No such loss versus frequency curves were provided by LLN or LVN, although they did show the dependence of their loss estimates (designated as  $\epsilon''$ ) on temperature.<sup>4</sup>

Although the LLN measurements of the ac response of NaCl are not the first for this material,<sup>10</sup> their analysis in terms of constant-loss dielectric response is apparently unique for it. It is more common to analyze the response of such materials at the impedance ( $Z \equiv Y^{-1}$ ) or complex modulus ( $M \equiv i\omega C_c Z$ ) levels, an approach pioneered for solid and liquid electrolytes by Armstrong *et al.*,<sup>11,12</sup> Bauerle,<sup>13</sup> and Ambrus, Moynihan, and Macedo.<sup>14</sup> For a material with blocking electrodes, external measurements cannot distinguish between displacement and conduction currents; thus, one must usually decide whether it is more appropriate to analyze results in terms of a dielectric or a

conduction process by using knowledge of the material and assessing the plausibility of the results of such different analyses.<sup>15,16</sup>

LVN concentrated their attention on the  $\epsilon''(\omega)$  part of their data and mentioned that the  $\epsilon'(\omega)$  part was relatively uninteresting;<sup>4</sup> but, for NaCl and probably for most of the other materials investigated by LLN and LVN,  $\Delta_c\epsilon'(\omega)$  data can contain a hidden universe of possibilities, exposed by accurate estimation of  $C_0$  and subsequent subtraction of its effects.  $\Delta_c\epsilon''(\omega)$  and  $\Delta_c\epsilon'(\omega)$  are associated parts of a Kronig-Kramers (KK) dispersion pair and neither should be considered unimportant.

LLN,<sup>1</sup> Lee *et al.*,<sup>3</sup> and LVN<sup>4</sup> have been rightly concerned that although constant loss at the dielectric level associated with dielectric dispersion implies a wide uniform distribution of activation energies<sup>15-18</sup> (appropriate for highly disordered systems), such a distribution is highly unlikely for a lightly doped single crystal. They thus conclude that none of the models presented in the literature provides a satisfactory explanation of their measurements. Not only does this problem entirely disappear when the dispersion effects are instead taken to arise from conductive rather than dielectric dispersion, as in the present work, but only  $\gamma$  values below unity are needed to describe the data, and only narrow activation energy distributions are present.

In the following sections, various conductive-system fitting models are considered; complex least-squares and spline fittings are carried out; and useful new conclusions are derived from the results of the analyses.

## II. PRELIMINARY ANALYSIS OF THE DATA

### A. Fitting models and some complex nonlinear least-squares-fitting results

Although ideally the NaCl data should be fitted to a model based on a detailed analysis of atomic transport processes operating in the solid, no such models are appropriate here. Two excellent complementary reviews containing detailed discussion of a variety of ac hopping conduction models have recently appeared.<sup>8,19</sup> Although these models, such as that following from the effective medium approximation or the jump relaxation approach,<sup>8</sup> usually deal with microscopic behavior and lead to approximate power-law frequency response, they provide no prediction of the temperature dependence of  $\gamma$ . By contrast, an exponential distribution of transition rates (EDTR) model does both but is semimacroscopic.<sup>17,18,20,21</sup> Thus, here we shall only employ empirical fitting models which, however, can lead to frequency response nearly identical to that of the more complicated EDTR.<sup>15,16,18</sup>

The basic empirical model used herein is that of Havriliak and Negami (HN), originally proposed at the dielectric response level,<sup>22</sup> but when written for conductive response it is just<sup>16</sup>

$$Y_{\text{HN}}(\omega) = G_0 [1 + (i\omega\tau_0)^\gamma]^\beta, \quad (4)$$

where  $0 < \beta < 1$ , and where  $0 < \gamma < 1$  is usually required as well.

Since, in the most general case, it is possible for a material to exhibit simultaneously dielectric dispersion associated with a normalized response function  $I_D(\omega)$ , and conductive-system dispersion described by the normalized response function  $I_C(\omega)$ , it is worthwhile to start with a general expression containing both effects. These response quantities are normalized so that they approach zero in the high-frequency limit and unity in the low-frequency limit.<sup>17</sup> In the most general case, each may involve more than a single dispersion process, but only one process for each need be considered here. Then, for example,  $I_C$  might be given by the  $(Y_{\text{HN}}/G_0)^{-1} \equiv (Z_{\text{HN}}/R_0)$  of Eq. (4), or a possible expression for  $I_D$  might be of the same form but defined, of course, at the complex dielectric constant level. At the admittance level, one finds<sup>16</sup>

$$Y(\omega) = (R_\infty + \Delta R I_C)^{-1} + i\omega(C_\infty + \Delta C I_D), \quad (5)$$

where  $\Delta R \equiv R_0 - R_\infty$ ;  $\Delta C \equiv C_0 - C_\infty$ ;  $R_0$  and  $C_0$  are low-frequency-limiting values; and  $R_\infty$  and  $C_\infty$  ( $\equiv \epsilon_\infty C_0$ ) are high-frequency-limiting values: the high-frequency bulk resistance and the geometric capacitance. For the present situation, fitting results obtained with simultaneously possible dielectric and conductive-system dispersion showed that dielectric dispersion was negligible, so  $I_D = 1$ .

With  $I_D = 1$ , what conditions are necessary to yield a result similar to that of Eq. (1)? Take  $R_\infty = 0$ ; then one obtains from Eq. (5)

$$Y(\omega) = G_0 \text{Re}(1/I_C) + i[G_0 \text{Im}(1/I_C) + \omega C_0], \quad (6)$$

a very general result when only conductive-system dispersion is present and  $R_\infty = 0$ . Now, specifically, take  $I_C^{-1} = (Y_{\text{HN}}/G_0)$  in Eq. (6) and set  $\beta = 1$ . The result may be written

$$Y(\omega) = G_0 + G_0(\omega\tau_0)^\gamma \cos(\psi) + i[G_0(\omega\tau_0)^\gamma \sin(\psi) + \omega C_0], \quad (7)$$

where  $\psi \equiv \pi\gamma/2$ . It follows that when  $\gamma = 1$ , there is no dispersion contribution to  $Y'$  analogous to the  $a\omega^\gamma$  term of Eq. (1), but there is a dispersion term in  $Y''$  which is very small for the present data since  $G_0\tau_0 \ll C_0$ .

However, Eq. (1) is not entirely physically realizable<sup>23</sup> because it formally applies all the way to infinite frequency and sets no limit to the possible value of  $\gamma$ . Even when  $s = \gamma = 1$  over a nonzero range of frequencies, this range must be finite. Then, the KK relations require that the imaginary part of the ac response, here  $(\omega\tau_0)G_0$ , must have a nonzero real part associated with it. Similarly, if only the real part has been determined experimentally, there must be a corresponding imaginary part whether  $\gamma < 1$  or  $\gamma > 1$ . Such paired response for  $\gamma > 1$  depends on the details of the cutoff at high frequencies and will be discussed in more detail elsewhere.<sup>24</sup>

Formally, the real part can be obtained from data with  $s = \gamma = 1$  by calculating  $\Delta_G Y'(\omega) \equiv Y'(\omega) - G_0$ ; but, because of the small magnitude of  $(\omega\tau_0)G_0$  for the present data,  $\Delta_G Y'(\omega)$  turns out to be very much smaller than  $G_0$  over much of the measured frequency range. Thus, unless one has available both accurate data and a close estimate of

the true value of  $G_0$ ,  $\Delta_G Y'(\omega)$ , the small difference between two nearly equal numbers, will be very uncertain. Then the conductive-system dielectric increment associated with the  $\Delta_G Y'(\omega)$ ,

$$\Delta_c \epsilon'' \equiv \Delta_G Y'(\omega) / (\omega C_c),$$

will also be quite small and error prone (see Sec. III C and Fig. 5).

In the present work, we shall examine three approximate ways of analyzing  $Y(\omega)$  and  $\Delta_{CG} Y(\omega)$  response by least-squares fitting. A defect of Eq. (1) is that it deals only with the real part of ac dispersion behavior, completely ignoring the related imaginary part. Much more information can be extracted from relaxation data, as demonstrated herein, when both parts are simultaneously used to fit an appropriate model. To begin with, let us generalize Eq. (1) to

$$Y(\omega) = G_0 + A\omega^\gamma + i\omega C_T, \quad (8)$$

where the frequency-independent quantity  $C_T$  is taken larger than  $C_0$  in order to take some very approximate account of the small, nearly capacitive contribution associated, through a KK relation, with the real-part dispersion term  $A\omega^\gamma$  when  $\gamma$  is nearly unity.

All frequency response fitting needed for the present work has been carried out using the readily available LEVM complex nonlinear least-squares (CNLS)-fitting program<sup>25</sup> running on an IBM-compatible PC. For these fits, which allow simultaneous fitting of both real and imaginary parts of the response, proportional weighting or power-law weighting, appropriate for data whose range is large,<sup>25,26</sup> was used.

CNLS fitting of the NaCl data with Eq. (8) yielded the following estimates for  $\gamma(T)$ : (a) 1.003|0.003; (b) 0.968|0.005; (c) 0.992|0.003; (d) 1.030|0.008; and (e) 1.045|0.010, where the letters denote the temperature as listed in the caption of Fig. 1. Meaningless estimates of  $\gamma$  were obtained for the (f), (g), and (h) temperature fits because of the strong dominance of the  $G_0$  contribution over most of the frequency range at these high temperatures. Nevertheless, the fits generally appeared good, and the solid lines in Fig. 1 were calculated from the present fit results; but, remember that these are log-log curves, a form of presentation that can conceal a variety of incongruities.<sup>15</sup>

Here and elsewhere, quantities shown in the form  $P|Q$  represent a parameter estimate and its estimated relative standard deviation (RSD). Parameter estimates are completely unreliable unless their corresponding  $Q$  is appreciably less than unity. Even when  $Q < 0.1$ , the estimates may still be unreliable, however, because of the presence of bias associated with systematic errors arising, for example, from an inadequate fitting model choice. Here, the actual relative residuals following from the fits at different temperatures were not entirely randomly distributed, indicating the presence of significant systematic errors. Thus, Eq. (8) is not a very satisfactory fitting model.

Nevertheless, fitting with Eq. (8) showed that  $G_0$  was thermally activated and that the (b)–(e) estimates of  $A$

were all nearly consistent, within one or two of their standard deviations, with a constant value. This requires that  $\tau_0^{-\gamma}$  must also be thermally activated with an activation energy close to that of  $G_0$ . This is a common finding, at least to first order, and is the basis for the Barton–Nakajima–Namikawa (BNN) relation<sup>27–30</sup> for ionic glasses, discussed and generalized in Sec. III A.

Since the true relative errors of the  $\gamma$  estimates cited above are undoubtedly larger than indicated by their present RSD values, the hypothesis that  $\gamma = s = 1$  for the first five data sets cannot be rejected based on these fitting results; but, least-squares fitting only gives a weighted averaged value of  $\gamma$  over the frequency range of the data, and the  $\gamma$  value for data set (b) is certainly somewhat different from unity in any case. Thus, a more appropriate fitting model is needed, and further CNLS-fitting results are presented in a later section. First, however, it is of interest to examine the actual log-log slopes of the  $Y'(\omega)$  data.

## B. Spline fitting and smoothing

We can directly test the validity of the power-law assumption by calculating actual frequency-dependent log-log slopes. Unfortunately, this valuable procedure has been very little used in the past.<sup>19</sup> Here, we have employed a generalized cross-validatory (GCV) spline-fitting, smoothing, and differentiation program.<sup>31</sup> It carries out a regularized least-squares spline fit with automatic determination, from the character of the data, of an appropriate degree of smoothing. Alternatively, the degree of smoothing can be set as an input choice. The smoothed results are then employed to calculate derivative values at desired points (the original frequencies and/or interpolated values between them). The use of quintic or heptic splines avoids end-point problems, even for the first derivative of the data. Such fitting gives an excellent estimate of the slope at each data point and at interpolated values.

The automatic GCV determination of appropriate smoothing incorporated in the present spline program assumes that the data contain additive, uncorrelated noise. But for data of the present type whose magnitudes usually span several decades, the dominant random errors are most likely to be approximately of proportional rather than additive character; but, such errors, if they are not too large, become closely additive when a logarithmic transformation of the data is carried out. Comparison of spline fitting results using untransformed and transformed data confirms the superiority of the latter procedure for the present data. Since we are interested in log-log slopes in any case, all spline-fitting results were calculated in this way.

Figure 2 shows unsmoothed log-log slopes,  $s_T(\omega)$ , for the full  $Y'(\omega)$  uninterpolated data. The curves in Fig. 2 are quite instructive and illustrate graphically the danger of concluding much about slopes from visual examination of such curves as those of Fig. 1. These results suggest that slope estimates of the present type should be calculated for similar data as a matter of course in future, since they not only provide information about the frequency where the total slope departs appreciably from zero, but they also

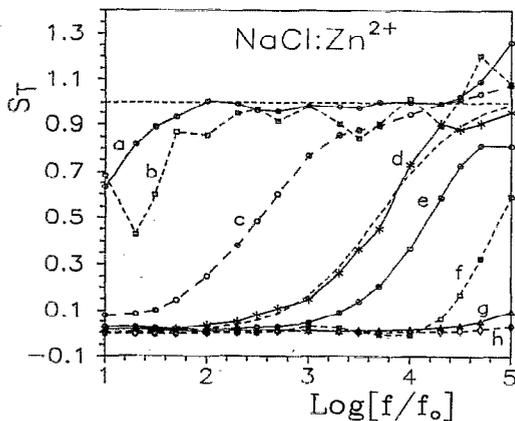


FIG. 2. Slopes of the log-log curves of Fig. 1 obtained by quintic spline fitting. To guide the eye, straight lines connect adjoining values at the spline knots. The scale factor  $f_0=1$  Hz.

provide some idea of the regularity of the original  $Y'$  or  $\sigma'$  data. Here they show that only for curve (a) (296.2 K) is  $s_T$  quite close to unity over an appreciable frequency range. Further, they indicate that at high frequencies the local slope can reach and even appreciably exceed unity. Now, although it is clear that the  $s_T$  slopes are not all constant and equal to unity, what about the frequency power-law exponent  $\gamma$ ? The dotted line associated with curve (d) in Fig. 2 was calculated from the  $d$  data CNLS fit results discussed in the previous sub-section and should be compared with the slope curve for the actual  $d$  data. Note that although the  $\gamma$  fit estimate was 1.03, the actual high-frequency-end values of  $s_T$  do not exceed 0.95.

Figure 3 presents the results of spline estimation of  $s(\omega)$  for the five lowest-temperature data sets. The  $G_0$  values employed are listed in the figure caption and were selected in a Bayesian fashion to try to make the low-

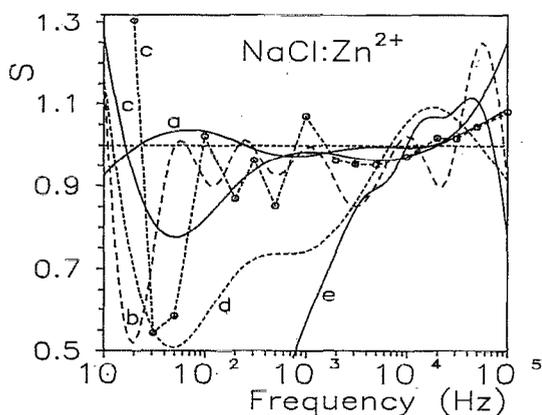


FIG. 3. Heptic-spline GCV smoothing-estimates of  $s$  for the five lowest temperatures. (See the Fig. 1 caption for temperature-letter identification.) The following  $G_0$  values were subtracted before spline fitting: (a)  $2.86 \times 10^{-14}$ , (b)  $8.00 \times 10^{-14}$ , (c)  $3.75 \times 10^{-12}$ , (d)  $7.70 \times 10^{-11}$ , and (e)  $4.56 \times 10^{-10}$  S. For comparison with these GCV smoothing results, the dashed curve marked (c) connecting circular points shows the results of an unsmoothed heptic-spline fit of the 17 original data points for this temperature.

frequency results come reasonably close to the higher-frequency ones. These  $G_0$  values were not much different from those obtained in the CNLS fit except for curve (b) Here, the spline fit results were interpolated to yield 81 points across the frequency range and therefore seem smoother than those in Fig. 2. Such interpolation does not, however, change the original GCV smoothing but just adds consistent points between the original smoothed values. These results again show that  $s$  and  $\gamma$  may be quite different. Although there is clearly a tendency for  $s$  values to be relatively close to unity for the lower-temperature results, the claimed new universality of LLN, which specifies  $\gamma=1$  over the range from 298 to 475 K, is certainly not verified by the present results.

### C. Nondispersed capacitive temperature response

The need to obtain accurate estimates of  $C_0$  and  $G_0$  has already been discussed. To do so, one must use a more appropriate fitting model than that of Eq. (8). It turns out that maximally accurate estimates can be obtained even when such a model is initially unknown. The approach is to fit the data to an equivalent circuit composed of the  $G_0$  and  $C_0$  elements in parallel with each other and in parallel with  $N$  additional branches, each made up of a resistor and capacitor in series. By making  $N$  sufficiently large, the ac part of the response, thus modeled as a distribution of relaxation times (DRT), can be approximated within the accuracy of the data themselves, allowing very precise estimates of  $G_0$  and  $C_0$  to be obtained. Such fitting has been carried out for smoothed and interpolated data using the LEVM program with  $N=11$ . Interpolation to yield many more effective data points than originally measured is required here since 24 fit parameters are estimated. This approach leads, even for the present noisy data, to estimates of  $C_0$  whose RSDs are less than  $10^{-4}$ , but even such precise estimates are hardly always accurate enough to yield good results after subtraction. This fitting method also allows useful estimates of the imaginary part of dispersion response to be obtained when only the real part is available and vice versa.<sup>24</sup>

Let us now briefly consider the nondispersed bulk capacitive/dielectric response of the present system. The value of the cell constant,<sup>2</sup>  $l/A$ , measured at room temperature, leads to a value of the empty-cell capacitance  $C_c$  of about 0.3833 pF. To first order,  $A/l$  should increase linearly with temperature because of thermal expansion. The value of the one-dimensional thermal-expansion coefficient for pure NaCl is about<sup>32</sup>  $4 \times 10^{-5}$ , leading to the following expression for  $C_c$ :

$$C_c \approx 0.3788(1 + 4 \times 10^{-5}T) \text{ pF}, \quad (9)$$

where  $T$  is the absolute temperature.

The excellent estimates of  $C_0$ , obtained as above, show clear, but small, temperature dependence. Because there is some uncertainty in the temperature values for the LLN data, it is most appropriate to fit  $C_0(T)$  using an errors-in-variables approach<sup>33,34</sup> which allows the uncertainties in  $T$  as well as those in the dependent variable to be taken into

account simultaneously. For the five lowest-temperature values of  $C_0$ , such a fit, which involved proportional weighting for the  $C_0$  dependent-variable values, yielded

$$C_0 = 2.493(1 + 3.81 \times 10^{-4}T) \text{ pF}, \quad (10)$$

with an exceptionally small  $S_F$  value for the fit of less than  $5 \times 10^{-4}$ , where  $S_F$  is a dimensionless quantity that measures the standard deviation of the relative residuals of the fit<sup>25,26</sup> when proportional weighting is employed. For comparison, good CNLS fits of typical relaxation data usually yield  $S_F$  values of the order of 0.01–0.05.

When fitting was carried out at the  $\epsilon$  level, using Eq. (9) for data conversion, the result for the low-frequency-limiting value of  $\epsilon$ ,  $\epsilon_0$ , was

$$\epsilon_0(T) = 6.594(1 + 3.31 \times 10^{-4}T), \quad (11)$$

involving a temperature coefficient still nearly ten times greater than the linear thermal-expansion coefficient for the pure material. This non-Curie temperature dependence must be associated with impurity conduction, but needs a more complete explanation.

The predicted value of  $\epsilon_0$  at 290 K is here about 7.23, nearly 23% larger than the accepted value for pure NaCl at this temperature, 5.90, which was determined by an electrodeless method.<sup>35</sup> It is likely that most of this difference is associated with a larger effective electrical area of the electrodes than the geometrical area. Discrepancies of this type of up to four times have been observed<sup>12</sup> for AgBr samples with nonblocking electrodes, but later work<sup>36</sup> indicated an excess of only 12% for this material, and measurements of AgCl showed about a 42% excess.<sup>37</sup> Thus, one should not balk at the present 23% difference, but it is a reason why the present work deals primarily with conductance rather than conductivity, just to eliminate further uncertainty. Note that the size of the present  $\epsilon_0$  is such that it cannot be confused with the  $\epsilon_\infty$  of pure NaCl, about 2.33 as determined from refractive-index measurements.<sup>35</sup> Finally, an  $\epsilon_0$  estimate such as that obtained here may be used to calculate  $\sigma_0$  values more accurately by allowing one to correct for the difference between the geometrical cell constant and its effective value.

### III. CONDUCTIVE DISPERSION

#### A. Final fitting model and BNN relations

In order to obtain an empirical fitting model which can describe full conductive-system dispersion efficiently with only a few free parameters, Eq. (5) with  $I_D=1$  is again appropriate, but now  $R_\infty$  is not set to zero and a variant of the Eq. (4) HN expression is used for  $I_C$ . The result is

$$Y(\omega) = [I_C^{-1}/(\Delta R + R_\infty I_C^{-1})] + i\omega C_0, \quad (12)$$

where

$$I_C^{-1} = \{1 + [i\omega(\Delta R C_\tau)]^\gamma\}^\beta. \quad (13)$$

Here,  $C_\tau$  is a new capacitance expected to show little or no temperature dependence, and the term in parentheses in Eq. (13) is just the  $\tau_o$  of Eq. (4). Note that when  $\gamma=\beta=1$  and  $R_\infty=0$ , the result is just single-relaxation-time Debye

response, that for a resistor  $\Delta R$  in parallel with a capacitance  $C_\tau$ , but one still does not obtain  $\omega^1$  power-law behavior for  $Y'(\omega)$ .

Although  $\tau_o$  has previously been expressed as a product of a thermally activated resistance and an unactivated capacitance,<sup>17</sup> the specific choice of the present  $\Delta R$  for the resistor is novel.  $\tau_o$  is written in the present form both because doing so greatly reduces the high correlation otherwise found between  $\Delta R$  and  $\tau_o$ , a change important in obtaining a good fit, and because the relative constancy of the  $A$  parameter estimates found from the Eq. (8) fits is strong evidence that a form of the BNN relation is applicable to the present data. This relation, expressed conventionally, is

$$G_0/C_c = \sigma_0/\epsilon_V = p(\epsilon_0 - \epsilon_\infty)\omega_p, \quad (14)$$

where  $p$  is a temperature-independent constant of order unity and  $\omega_p$  is the dielectric-loss peak frequency. The constancy of  $p$  implies that  $G_0$  and  $\omega_p$  must have nearly the same temperature dependence when Eq. (14) is applicable.

Two modifications of Eq. (14) seem worthwhile. First,  $\omega_p$  is most appropriate for symmetrical response, where it is equal to  $\tau_o^{-1}$ . For either symmetric or asymmetric response, it is thus likely to be better to use the actual CNLS fitting value of  $\tau_o$  rather than a peak frequency, usually estimated graphically from noisy data. Second, and most important, there is no reason to expect that  $R_\infty$  and  $\Delta R$  should have the same activation energy (see Sec. III D). Thus,  $G_0$ , which is equal to  $(R_\infty + \Delta R)^{-1}$ , provides less information than do  $R_\infty$  and  $\Delta R$  separately. If we therefore replace the  $G_0$  in Eq. (21) by  $(\Delta R)^{-1}$  (a measure of the dispersive strength of the conductive-system response),  $\omega_p^{-1}$  by  $\Delta R C_\tau$ , and  $p$  by a new constant  $q$ , we obtain just

$$\epsilon_\tau \equiv C_\tau/C_c = q(\epsilon_0 - \epsilon_\infty), \quad (15)$$

a simple form which involves only quantities with small temperature dependence.

However, neither the conventional BNN relation nor Eq. (15) should be expected to apply to conductive-system response where the ac dispersion is not independent of  $G_0$ . In the present situation, we deal with the very small conductive-system dielectric increment,  $\Delta_c \epsilon'(\omega)$ , rather than with  $(\epsilon_0 - \epsilon_\infty)$ . When the form of the fitting model is known, one can directly calculate an equation analogous to Eq. (15) by considering response as  $\omega \rightarrow 0$ . For the present situation, calculation of  $\Delta_c \epsilon'$  from Eqs. (12) and (13) with  $\beta=1$  leads to

$$C_\tau^\gamma/C_c = q_c [\omega^{1-\gamma} \Delta_c \epsilon'(\omega)]_{\omega \rightarrow 0}, \quad (16)$$

where  $q_c$  takes the place of the above  $p$  or  $q$  and is given by

$$q_c \equiv [R_0/(\Delta R)^\gamma] \csc(\psi). \quad (17)$$

At sufficiently low limiting frequency, physical realizability requires<sup>23</sup> that  $\Delta_c \epsilon'(\omega)$  approach a constant nonzero value,  $\Delta_c \epsilon'(0)$ , contrary to the prediction of Eq. (13) for  $\beta=1$  and  $\gamma < 1$ . Then, in fact, effectively  $\gamma=1$ , and we may write

$$\epsilon_\tau = [1 + (R_\infty/\Delta R)] \Delta_c \epsilon'(0). \quad (18)$$

TABLE I. Results of nonlinear least-squares fits of  $\Delta_C Y(\omega)$  to a conductive-system response function.

$T$ (K)	$S_F$	$C_0$ (pF)	$R_\infty$ ( $\Omega$ )	$\Delta R$ ( $\Omega$ )	$10^{14}C_T$ (F)	$\gamma$ ( $\beta$ )	
a	296.2	0.034	2.757 0.0018	$6.96 \times 10^5$  0.04	$1.754 \times 10^{14}$	3.38 0.002	0.9742  $1.2 \times 10^{-4}$
b	328.7	0.034	2.793 0.0066	$1.85 \times 10^5$  0.17	$8.162 \times 10^{12}$  0.057	2.72 0.009	0.9496  $7.410^{-4}$
c	363.2	0.012	2.809  $5 \times 10^{-4}$	$4.63 \times 10^5$  0.04	$2.580 \times 10^{11}$  0.003	4.42 0.001	0.9663  $9.6 \times 10^{-5}$
c	363.2	0.050	2.839  $3 \times 10^{-5}$	$1.56 \times 10^8$  0.04	$2.317 \times 10^{11}$  0.016	1.47 0.010	(0.832  $2.1 \times 10^{-3}$ )
d	400.7	0.026	2.879  $2 \times 10^{-5}$	$1.98 \times 10^8$  0.02	$1.258 \times 10^{10}$  0.005	1.13 0.004	0.827  $1.5 \times 10^{-3}$
e	429.2	0.023	2.906  $3 \times 10^{-5}$	$1.08 \times 10^8$  0.02	$1.998 \times 10^9$  0.004	1.56 0.004	0.859  $1.6 \times 10^{-3}$

As expected, here Eq. (16) with  $q_c$  of the order of unity, rather than Eq. (15), is indeed satisfied by the present data at the lowest measured frequencies.

## B. More CNLS fitting results

Table I presents the results of fitting the lower-temperature NaCl data with the conductive-system model for  $Y(\omega)$  discussed above. Fitting was carried out at the admittance level and used proportional or power-law weighting.<sup>25,26</sup> At temperatures above 429.2 K, there is not sufficient ac response present to allow reasonable dispersion results to be found. Fit estimates were comparable whether one fitted with all five parameters free or whether accurate  $C_0$  values were first subtracted to obtain  $\Delta_C Y(\omega)$  and such transformed data then fitted without  $C_0$  in Eq. (12). However, subtraction using an inappropriate value of  $C_0$  led to  $\Delta_C Y$  values whose real and imaginary parts were not an accurate KK pair and, as usual for the present data, even a very small change in the subtracted value of  $C_0$  was found to produce large effects in the result. A test that subtracted data actually represents dispersion response is the ability to obtain a good fit of the model (which is intrinsically KK consistent), with nearly the same parameter estimates for fitting at both the admittance and impedance levels. For proportional weighting, fitting at the impedance level yields exactly the same estimates as does that at the complex modulus level. Note that the first  $C_0$  value for  $T=363.2$  K does not lie closely on a smooth curve with the other values and, unlike the other values listed, does not agree closely with those found by DRT fitting (see Sec. II C). To throw some light on this anomalous situation, two rows of results are included for this data set.

All exponent estimates shown in the last column of Table I are for  $\gamma$  free and  $\beta$  fixed at unity except that in the fourth row where the situation is reversed. Although best fits after subtraction were obtained for the present data sets when  $\beta$  was fixed at unity and  $\gamma < 1$ , the second 363.2 K line was obtained with  $\gamma$  set to unity and  $\beta < 1$ . The latter fit was appreciably worse than the former, as shown by the corresponding  $S_F$  values, quantities which here measure the relative standard deviation of the overall fit.<sup>25,26</sup> Although the first of the two fits yielded an implausible estimate of  $C_0$ , the rest of its predictions seem reasonable when compared to those for lower temperatures. On the other hand, the second fit gave an excellent estimate for  $C_0$  and led to other results which seem reasonable when compared to those for the two higher temperatures.

Although the resolution limit of the LEVM CNLS-fitting program<sup>38</sup> may be approached at the lower temperatures where the ratio  $\Delta R/R_\infty$  can be as large as  $10^8$ , the analysis of Sec. III D below suggests alternatively that even the small estimates of  $R_\infty$  found at the two lowest temperatures are still significant, and that the problem with obtaining consistent results at  $T=363.2$  K is associated with a real, relatively abrupt change in the behavior of the response near this temperature. Incidentally, the present inclusion of  $R_\infty$  in Eq. (12) used for fitting led to far better results than its omission and replacement by a separate electrode resistance added in series with the rest of the circuit at the impedance level. Thus,  $R_\infty$  represents a true bulk effect rather than an electrode effect.

The value of  $\Delta R$  for  $T=296.2$  K shown in Table I was taken fixed in the fitting for this temperature since it could not be reliably estimated for this very high-resistance situation. The value used is that obtained from the DRT fitting discussed above, but even there it was very uncertain. The alternative use in the fitting of  $\Delta R=3.8 \times 10^{14} \Omega$ , the value obtained by extrapolation from higher-temperature-fit estimates, led to negligible changes in the estimates of the other quantities at 296.2 K. Finally, although there is a considerable amount of variability evident in the  $C_T$  estimates, particularly at the lower temperatures where the data do not extend close to the  $\omega\tau_0=1$  region, such variability may be random and is, in any case, small compared to the thermally activated variation of  $\Delta R$ . The present fitting estimates suggest that the  $T=363.2$  K data represent a transition between lower-temperature response where  $\gamma$  is close to unity (nearly single-relaxation-time response), and higher-temperature behavior where there is a broader DTR and  $\gamma$  seems to remain nearly constant near 0.85.

## C. Impedance- and dielectric-level dispersion response

Figure 4 shows some impedance-plane conductive-system dispersion plots for  $T=400.7$  and 429.2 K. To compare results for different temperatures on the same scale, the data and fit results were normalized using the appropriate  $\Delta R$  values. The resulting  $Z_N \equiv 1/(\Delta R \Delta_C Y)$  quantities are not quite equal to  $I_C$  because they still contain small  $R_\infty$  effects. In the figure, the arrow shows the direction of increasing frequency and the asterisks indicate points at 1000 Hz. The dashed curve is a Debye semicircle and the points plotted on it are those for the lower tem-

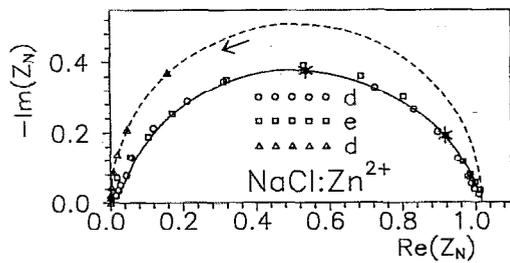


FIG. 4. Impedance-plane plots of impedances normalized with  $\Delta R$  to allow shape comparison for two temperatures. Triangular points are for  $T=400.7$  K data without subtraction of the effects of  $C_0$ , and the other points and solid-line curve include such subtraction using the  $C_0$  values of Table I. The solid-line curve is also for 400.7 K and shows the results of spline smoothing and interpolation. The asterisks indicate points at 1000 Hz.

perature without any  $C_0$  subtraction. In the past, bulk semicircles like this were nearly always found if the frequency range was appropriate. In most of the earlier work, however, the resistance level was much lower than it is here, so such a semicircle would only appear at much higher frequencies than those of the present data. In contrast, here appreciably lower frequencies than 10 Hz would be required to delineate the rest of the dashed curve. However, such essentially nondispersive bulk response, closely just that of  $R_0$  and  $C_0$  in parallel, is not of particular interest here.

The remaining parts of the figure show the real underlying dispersive response when the effect of  $C_0$  is subtracted at the admittance level and the results then converted to the impedance level and normalized. The circles and squares show the original (transformed) data points, and the smooth curve was plotted from the resulting splined/interpolated 400.7 K data. These data yielded the fit estimates presented in Table I for this temperature. We see that the shape of the results is nearly the same for the two temperatures, since the corresponding  $\gamma$  values in the table are not very different, but the 1000 Hz point for the higher temperature occurs much closer to the low-frequency end than does the other such point. Some of the lowest-frequency response data have been omitted from both curves (and from the fitting) for clarity and better fits.

These results and those of Table I confirm that the present NaCl data are best analyzed in terms of  $\gamma \neq 1$  conductive-system response at the impedance or complex modulus level rather than in terms of dielectric-system dispersion at the dielectric or admittance level; but, since LLN, LVN, and most workers in the present field have been primarily concerned with conductivity/dielectric-level response and have often contented themselves with analysis of  $\sigma_0$ ,  $\sigma'_{ac}(\omega) \equiv \sigma'(\omega) - \sigma_0$ , and the corresponding  $\Delta\epsilon''$  response, it is worthwhile to examine such a response as well. First, LVN have used<sup>4</sup> an expression derived by Pollack and Pike<sup>39</sup> to fit their  $\Delta\epsilon''(T)$  results. This expression, which includes several approximations, involves  $\omega^1$  dependence and is taken as a justification for their  $\gamma=1$  conclusion; but, the actual originators of this

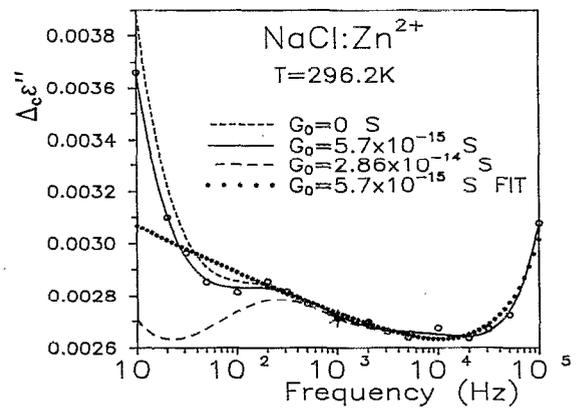


FIG. 5. The frequency dependence of  $\Delta\epsilon''$  for  $T=296.2$  K plotted on an expanded scale. The effects of subtracting several different  $G_0$  values are shown. The circles show the original transformed data, with the point at 1000 Hz denoted by an asterisk, and the dotted curve is the theoretical prediction following from the conductive model and the appropriate parameter estimates presented in Table I.

expression speak only of “approximate”  $\omega^1$  dependence. Further, Austin and Mott,<sup>40</sup> in a somewhat similar treatment find that  $\gamma$  is usually of the order of 0.8. In addition, later treatments<sup>5,6</sup> yield expressions for  $\gamma$  which only approach unity from below in the low-temperature limit. The EDTR model for a conducting system<sup>16-18</sup> also leads to such a response.

It is sufficient to show the  $\Delta\epsilon''$  vs  $\omega$  curve for  $T=296.2$  K, since the present slope results confirm that this temperature yields the closest approach to  $s(\omega)=1$  behavior. In Fig. 5, smoothed-data results have been plotted on an expanded scale. The  $G_0$  values shown on the graph are those subtracted to form  $\Delta\epsilon''$ . The fitting model for this temperature used  $G_0=5.7 \times 10^{-15}$  S, and this value was subtracted from the  $Y$ -level model predictions to obtain the dielectric-level fit curve shown dotted on the figure. The points denoted by circles represent the original unsmoothed (but transformed) data for this temperature. It is evident that the conductive-system model does a good job of representing the main details of the response at this level. If  $R_\infty$  is omitted, the fit becomes appreciably worse, especially at the higher frequencies. Note that the  $\gamma$  fitting estimate, 0.974, is not equal to unity, and that the model predicts small but regular departures from frequency-independent  $\Delta\epsilon''$  behavior, dependence inconsistent with exact  $\gamma=s=1$  behavior; again, the LNN conclusion that  $\gamma=1$  must be rejected.

In their later work,<sup>4</sup> LVN have proposed an expression for  $\sigma'(\omega)$  which is the sum of  $\sigma_0$  and two power-law terms, one with a value of  $\gamma$  of unity and the other with  $\gamma \sim 0.6$ . They assume that the coefficient of their  $\omega^1$  term,  $A'$ , is not thermally activated. The present work suggests that a value of  $\gamma=s=1$  is unsupported by both theory and experiment, and we have already seen that the lack of apparent activation of the  $A'$  coefficient is a likely consequence of the BNN relation associated with near-equal activation energies for  $\sigma_0$  and  $\tau_0^{-1}$  for conductive-system response.

Although the present conductive-system fitting model

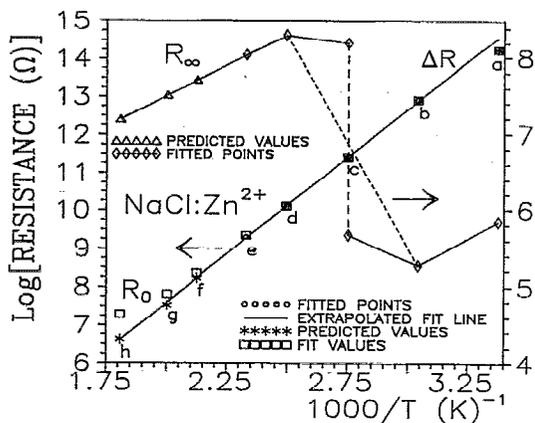


FIG. 6. Arrhenius plots of the conductive-model resistances  $R_\infty$ ,  $\Delta R$ , and  $R_0$ . The predicted values of  $\Delta R = R_0 - R_\infty$  (asterisks) for temperatures (f), (g), and (h) used the fit values (squares) of  $R_0$  and the following  $R_\infty$  values (triangles): (f)  $5.03 \times 10^7$ ; (g)  $3.17 \times 10^7$ ; and (h)  $1.52 \times 10^7 \Omega$  which were extrapolated from the (d) and (e)  $R_\infty$  fit estimates. The  $\Delta R$  values for temperatures (b), (c), (d), and (e) were obtained directly from CNLS fitting (see Table I).

has been shown to be quite adequate for most of the present data, the low-frequency region where  $\omega\tau_0 \ll 1$ , particularly dominant for the present data at the higher temperatures, probably involves some electrode-impedance effects, which are often modeled by a constant-phase element.<sup>41</sup> It is likely that the power-law term with  $\gamma \sim 0.6$  proposed by LVN is needed to help model such electrode contributions to the total response, but a more complete analysis would not assume such a response *ab initio*. Instead, for conductive systems such as those considered here and by LLN and LVN one would use CNLS fitting to establish an appropriate  $I_C$  response function to represent higher-frequency response and to find an appropriate expression to model the series contribution of electrode-impedance effects at the lower frequencies. Such an expression might well involve finite-length diffusion response,<sup>41,42</sup> which involves  $\gamma = 0.5$  behavior over part of its range.

#### D. Resistive temperature dependences

Figure 6 shows some Arrhenius-plot results obtained by proportional-weighting nonlinear least-squares fitting<sup>26</sup> of

$$\Delta R(T) = BT^n \exp(E_{\Delta R}/kT), \quad (19)$$

to the four b–e estimates given in Table I, with the first, rather than the second,  $T = 363.2$  K value used. A similar expression was used for  $R_\infty$  fits. Here  $B$  is a temperature-independent constant. The quantity  $n$ , which is usually taken<sup>43,44</sup> as 1 or 0, was set equal to unity here. First, the  $\Delta R$  fit estimates for temperatures b, c, d, and e were used with Eq. (19) to obtain the following estimated value of  $E_{\Delta R}$ : 0.976|0.011 eV. The  $\Delta R$  solid line in Fig. 6 is an extrapolation over the full measured temperature range of the four-point fit results. Since  $R_\infty$  is not dispersed but is a high-frequency-limiting quantity, it is reasonable to iden-

tify  $E_{\Delta R}$  as a measure of the conduction activation energy, involving both association and migration (mobility, percolation) effects.

Although the corresponding estimated conductivity activation energy, calculated taking account of the small temperature dependence of  $C_c$ , Eq. (9), is not significantly different from the above  $E_{\Delta R}$  value, this is because here  $\Delta R \gg R_\infty$  over most of the fit range. However, for conductive-system dispersion when  $R_\infty \neq 0$ , it is  $\Delta R$  and  $R_\infty$  separately, not the combined quantities  $G_0$  ( $\equiv R_0^{-1}$ ) or  $\sigma_0$ , which are basic. This important distinction has evidently not been adequately appreciated before.

Next, the two d and e estimates of  $R_\infty$  were used to obtain an estimate of  $E_{R_\infty}$  of 0.281 eV. Then the difference,  $E_{\Delta R} - E_{R_\infty}$ , here about 0.695 eV, may reasonably be identified as the vacancy-migration activation energy  $E_m$ , associated with mobility/percolation processes. This estimate of  $E_m$  is very close, considering the rather meager numerical foundation of the calculation, to the accepted value of 0.69 eV for NaCl.<sup>45</sup> Over the temperature range of the present data the cation vacancies and dopant ions are highly associated,<sup>1</sup> and  $R_\infty$  must arise from the ac behavior of these quantities in nonpercolating states; but, in this highly associated region, the mass-action law may be used to show that  $E_{R_\infty} = E_a/2$ , where  $E_a$  is the actual association energy.

The thermal activation fit of the above two  $R_\infty$  estimates was then used to predict values of  $R_\infty$  for the three highest temperatures (values listed in the caption of Fig. 6) and the lowest one. Next, using these values and the  $R_0$  values calculated from the higher-temperature  $G_0$  values obtained from Eq. (8) fitting: (f)  $4.555 \times 10^{-9}$ |0.007, (g)  $1.543 \times 10^{-8}$ |0.056, and (h)  $5.18 \times 10^{-8}$ |0.21 S,  $\Delta R$  estimates were obtained and are plotted as asterisks. It is remarkable how closely the resulting high-temperature values fall on the extrapolated  $\Delta R$  line.

LLN obtained an estimate of  $E_\sigma = E_G = 0.95$  eV from fitting of  $\sigma_0$  values over nearly 5 decades.<sup>1</sup> The present  $R_0$  estimates are plotted as squares on the graph. Although they do not lie on a straight line, correction to yield high-temperature  $\Delta R$  estimates leads to a good  $\Delta R$  straight line over nearly 7 decades. These results further justify the introduction of a nonzero  $R_\infty$  in the present work and clearly show that for data of this kind, it is important to consider both  $R_\infty$  and  $\Delta R$  separately and to deal directly with resistive rather than conductive elements. An alternative to the above analysis approach is to use weighted nonlinear least-squares to fit all the present  $R_0$  estimates using a sum of two exponentials, each of the form of Eq. (19). With proportional weighting one obtains very nearly the same values for the  $\Delta R$  parameters as above and an estimate of  $E_{R_\infty}$  of 0.26|0.32 eV, a rather poorly defined but still somewhat significant value.

All the fit values of  $R_\infty$  are also shown in Fig. 6 along with the three predicted high-temperature values. Although the two different fit values for  $T = 363.2$  K are shown, this is not meant to indicate that both are simultaneously appropriate. Nevertheless, these  $R_\infty$  results show clearly that some kind of a transition occurs in  $R_\infty$  over a

relatively narrow temperature range near 363.2 K. It cannot be a glasslike transition because  $\tau_0$  approaches infinity for such a transition, and  $R_\infty$  does not even involve dispersion. When an estimate of  $E_{R_\infty}$  is alternatively calculated using the Table I  $R_\infty$  estimates for the two low temperatures a and b, one obtains 0.326 eV, not far different from the 0.281 eV estimate found above.

We can now suggest a tentative explanation for these new and surprising results. Although  $R_\infty$  is almost certainly a measure of the nonpercolating ac conduction arising from the motion of cation vacancies closely associated with impurity ions, its rapid increase above 350 K by a factor of nearly  $10^4$  suggests a structural change. The low-temperature branch of  $R_\infty$  quite likely involves vacancies moving around a dopant ion by occupying nearest-neighbor positions. Since the transition involves only a small change in activation energy from about 0.33 down to 0.28 or 0.26 eV, the great increase in  $R_\infty$  must be strongly dominated by a structural entropy increase, probably reflecting a change in vacancy-dopant clustering. The high-temperature branch may thus involve vacancies still bound to the dopant ion but probably occupying next-nearest-neighbor positions. If so, the small decrease in  $E_a$  apparent here when passing from below to above the transition is what one would expect theoretically.

Unfortunately, there seems to be little experimental information available in the literature on zinc-doped NaCl. The one reference found<sup>46</sup> involved much higher temperatures than those here and did not lead to an estimate for the association energy (enthalpy). However, this quantity has been calculated theoretically for zinc impurities in NaCl for both nearest- and next-nearest-neighbor states.<sup>47</sup> The results obtained were 0.78 and 0.75 eV, respectively. Although these estimates are somewhat larger than the present corresponding ones of about 0.65 and 0.56, they are qualitatively similar and, in any case, depend sensitively on the form of the potential used in the calculations. Finally, the present values are plausible when compared to experimental estimates for other dopant ions in NaCl.

It is reasonable to assume that a fraction of the vacancies which are bound to dopant ions now and then become free to percolate through the material with a migration activation energy  $E_m$  and are thus able to contribute to dc conduction. If so, their concentration should be proportional to that leading to  $R_\infty$ , explaining the presence of  $E_{R_\infty}$  in  $E_{\Delta R} = E_{R_\infty} + E_m$ . However, if this is the case, one might expect to see some effects of the  $R_\infty$  transition in the separate  $\Delta R$  estimates. We evidently do not do so because  $\Delta R$  is appreciably greater than  $R_\infty$ , because  $E_a$  does not change much through the transition, and because the free vacancy concentration must be largely independent of the specific clustering configuration leading to  $R_\infty$ . It is also significant that there is no observable effect of the  $R_\infty$  entropy transition in the temperature dependencies of  $C_0$  and  $\epsilon_0$ , Eqs. (10) and (11).

#### IV. CONCLUSIONS

A new fitting approach for conducting-system data is shown to describe well both the real and imaginary parts of

the present NaCl ac dispersion response in a self-consistent manner without dielectric dispersion contributions. Detailed analysis of the data yields no viable evidence for  $\gamma = s = 1$  over an appreciable frequency region using either direct slope determination or an appropriate fitting model. Instead, one finds  $\gamma$  estimates less than, but reasonably close to, unity at low temperatures (nearly single-relaxation-time response) and values possibly stabilizing near  $\gamma = 0.85$  for the higher-temperature region. Thus, the  $\gamma = 1$  "new universality" proposed by LLN does not apply to their NaCl data, and their identification of constant-loss dielectric response is actually only approximately frequency independent and arises not from dielectric dispersion but from conductive-system dispersion.

The present conductive-system analysis shows that for such systems one needs to include in a fitting model the possibility of both a high-frequency-limiting resistance (or resistivity)  $R_\infty$ , probably involving the association activation energy, and a differently activated resistance,  $\Delta R \equiv R_0 - R_\infty$ , representing the strength of the conductive-system dispersion. Both activation energies can be found, and in the present case their difference yields a very close estimate of the migration activation energy for cation vacancies. Since  $G_0$  ( $\equiv R_0^{-1}$ ) or  $R_0$  thus involves two different activation energies, they are not appropriate quantities for estimating a single such energy through Arrhenius plotting, especially at high temperatures where  $R_\infty$  becomes comparable to  $\Delta R$ .

In spite of the deficiencies of the present data, it has been demonstrated that detailed analysis is possible even when the most significant part of the data is obscured by much larger effects associated with low-frequency-limiting conductance and capacitance. Spline fitting/smoothing/interpolation has been shown to be a valuable tool in examining raw data, calculating frequency-dependent log-log slopes  $s(\omega)$ , and even allowing fitting procedures otherwise limited by too few available data points. An important conclusion is that such slope values should always be well distinguished from least-squares estimates of the frequency power-law exponent  $\gamma$ , since the latter is an average over a variety of possible measurement and model errors.

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  $\gamma$  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.

For electrically conducting systems, such as that considered here, analysis should be carried out primarily in terms of a model of dispersion at the impedance level rather than by assuming dielectric dispersion only. Complex nonlinear least-squares fitting can be used to help distinguish between the two types of behavior and can even show whether both are simultaneously present. Contrary to usual practice, it is crucial to not ignore the details of the

imaginary part of the admittance data (associated with the real part of the complex data at the dielectric level). Dispersion involves both a real and an imaginary part and one ignores either of them at risk of error.

## ACKNOWLEDGMENTS

I am very grateful to Professor A. S. Nowick and his group for their kindness in sending me their data on doped NaCl and for helpful information. I much appreciate the valuable suggestions of Professor G. Johari, Professor L. M. Slifkin, and Professor W. J. Thompson.

<sup>1</sup>W. K. Lee, J. F. Liu, and A. S. Nowick, *Phys. Rev. Lett.* **67**, 1559 (1991). In later work (Ref. 4), Lim, Vaysleyb, and Nowick have pointed out that measurements on doped NaCl are difficult to reproduce. Nevertheless, their original NaCl data represent the particular response of the material for a certain set of conditions and are thus worthy of detailed analysis, both for itself and to demonstrate the value of appropriate analysis methods.

<sup>2</sup>A. S. Nowick (private communication).

<sup>3</sup>W. K. Lee, B. S. Lim, J. F. Liu, and A. S. Nowick, *Solid State Ionics* **53-56**, 831 (1992).

<sup>4</sup>B. S. Lim, A. V. Vaysleyb, and A. S. Nowick, *Appl. Phys. A* **56**, 8 (1993); the citation to Ref. 15 on p. 13 of this work should be to Ref. 16.

<sup>5</sup>A. R. Long, *Adv. Phys.* **31**, 553 (1982); see Table 5.

<sup>6</sup>S. R. Elliott, *Adv. Phys.* **36**, 135 (1987); see Fig. 25.

<sup>7</sup>C. A. Angell, *Chem. Rev.* **90**, 523 (1990); see Fig. 20.

<sup>8</sup>K. Funke, *Prog. Solid State Chem.* **22**, 111 (1993); see additional references listed here.

<sup>9</sup>K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).

<sup>10</sup>S. Lanyi and K. Hricovini, *J. Phys. Chem. Solids* **44**, 905 (1983).

<sup>11</sup>R. D. Armstrong, W. P. Race, and H. R. Thirsk, *Electrochim. Acta* **13**, 215 (1968).

<sup>12</sup>R. D. Armstrong, T. Dickinson, and R. Whitefield, *J. Electroanal. Chem.* **39**, 257 (1972).

<sup>13</sup>J. E. Bauerle, *J. Phys. Chem. Solids* **30**, 2657 (1969).

<sup>14</sup>J. H. Ambrus, C. T. Moynihan, and P. B. Macedo, *J. Phys. Chem.* **76**, 3287 (1972).

<sup>15</sup>J. R. Macdonald, *J. Appl. Phys.* **62**, R51 (1987); *J. Appl. Phys.* **65**, 4845 (1989).

<sup>16</sup>J. R. Macdonald and J. C. Wang, *Solid State Ionics* **60**, 319 (1993).

<sup>17</sup>J. R. Macdonald, *J. Appl. Phys.* **58**, 1955 (1985).

<sup>18</sup>J. R. Macdonald, *J. Appl. Phys.* **61**, 700 (1987).

<sup>19</sup>M. P. J. van Staveren, H. B. Brom, and I. J. de Jongh, *Phys. Rep.* **208**, 1 (1991).

<sup>20</sup>J. R. Macdonald, *J. Appl. Phys.* **34**, 538 (1963).

<sup>21</sup>J. C. Dyre, *J. Appl. Phys.* **64**, 2456 (1988).

<sup>22</sup>S. Havriliak, Jr. and S. Negami, *Polymer* **8**, 161 (1967).

<sup>23</sup>J. R. Macdonald, *Solid State Ionics* **25**, 271 (1987).

<sup>24</sup>J. R. Macdonald (unpublished).

<sup>25</sup>J. R. Macdonald and L. D. Potter, Jr., *Solid State Ionics* **23**, 61 (1987); J. R. Macdonald, *Electrochim. Acta* **35**, 1483 (1990). The LEVM program, V. 6, is extremely comprehensive and includes many powerful features for accurate fitting of conductive- and dielectric-system frequency and time response data.

<sup>26</sup>J. R. Macdonald and W. J. Thompson, *Commun. Statistics Simulation Computation* **20**, 843 (1991).

<sup>27</sup>J. L. Barton, *Verres Refract.* **20**, 328 (1966).

<sup>28</sup>T. Nakajima, *1971 Annual Report, Conference on Electric Insulation and Dielectric Phenomena* (National Academy of Sciences, Washington DC, 1972), p. 168.

<sup>29</sup>H. Namikawa, *J. Non-Cryst. Solids* **18**, 173 (1975).

<sup>30</sup>J. C. Dyre, *J. Non-Cryst. Solids* **88**, 271 (1986).

<sup>31</sup>H. D. Woltring, *Adv. Eng. Software* **8**, 104 (1986).

<sup>32</sup>G. K. White, *Proc. R. Soc. London Ser. A* **286**, 204 (1965).

<sup>33</sup>J. R. Macdonald and W. J. Thompson, *Am. J. Phys.* **59**, 854 (1991).

<sup>34</sup>P. T. Boggs and J. E. Rogers, *Contemp. Math.* **112**, 183 (1990).

<sup>35</sup>R. Lowndes and D. H. Martin, *Proc. R. Soc. London Ser. A* **308**, 473 (1969).

<sup>36</sup>R. K. Rhodes and R. P. Buck, *J. Electroanal. Chem.* **86**, 349 (1978).

<sup>37</sup>R. P. Buck, D. E. Mathis, and R. K. Rhodes, *J. Electroanal. Chem.* **80**, 245 (1977).

<sup>38</sup>J. R. Macdonald, *J. Electroanal. Chem.* **307**, 1 (1991).

<sup>39</sup>M. Pollak and G. E. Pike, *Phys. Rev. Lett.* **28**, 1449 (1972).

<sup>40</sup>I. G. Austin and N. F. Mott, *Adv. Phys.* **18**, 41 (1969).

<sup>41</sup>*Impedance Spectroscopy—Emphasizing Solid Materials and Systems*, edited by J. R. Macdonald (Wiley-Interscience, New York, 1987).

<sup>42</sup>D. R. Franceschetti, J. R. Macdonald, and R. P. Buck, *J. Electrochem. Soc.* **138**, 1368 (1991).

<sup>43</sup>S. W. Martin and C. A. Angel, *J. Non-Cryst. Solids* **83**, 185 (1986).

<sup>44</sup>H. Jain and J. N. Mundy, *J. Non-Cryst. Solids* **91**, 315 (1987).

<sup>45</sup>F. Agullo-Lopez, C. R. A. Catlow, and P. D. Townsend, *Point Defects in Materials* (Academic, London, 1988), Chap. 5.

<sup>46</sup>S. J. Rothman, L. W. Barr, A. H. Rowe, and P. G. Sherwood, *Philos. Mag.* **14**, 501 (1966).

<sup>47</sup>C. Ruiz-Mejia, J. Hernandez N., J. Rubio O., and H. Murieta S., *Cryst. Lattice Defects Amorphous Mater.* **14**, 105 (1987).