

## Limiting Behavior of ac Conductivity in Ionically Conducting Crystals and Glasses: A New Universality

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The ac conductivity  $\sigma(\omega)$  of three ionically conducting crystalline materials (NaCl:Zn<sup>2+</sup>, KTaO<sub>3</sub>:Co<sup>2+</sup>, H<sup>+</sup>, and CeO<sub>2</sub>:Gd<sup>3+</sup>) and two glasses have been studied over an unusually wide temperature range. In all cases, limiting power-law behavior [exponent  $s=1$  in  $\sigma(\omega)=\sigma_0+A\omega^s$ ] is observed at relatively low temperatures. It is concluded that this limiting behavior is a universal phenomenon. Available theoretical explanations have been examined and found to be unsatisfactory.

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The ac conductivity of many materials shows dispersion behavior through a dependence of the electrical conductivity  $\sigma$  on angular frequency  $\omega$  of the form

$$\sigma(\omega) = \sigma_0 + A\omega^s, \quad (1)$$

where  $\sigma_0$  is the dc (or low-frequency) conductivity and the exponent  $s$  lies in the range  $0 < s < 1$ . Such behavior has been so widely observed for highly disordered materials, e.g., ionically conducting glasses, conducting polymers, and amorphous semiconductors, that it has come to be known as the "universal dynamic response" [1,2]. Other manifestations of this relaxation-type behavior appear in the real part of the dielectric constant,  $\epsilon'$ , which varies as

$$\epsilon' - \epsilon'_\infty \propto \omega^{s-1}, \quad (2)$$

where  $\epsilon'_\infty$  is the high-frequency value of  $\epsilon'$ . [Equation (2) follows from (1) as a consequence of the Kronig-Kramers relations.] In the time domain, Eq. (1) is equivalent to

$$\phi(t) = \exp(-t/\tau)^{1-s}, \quad (3)$$

where  $\phi(t)$  is the normalized decay of the transient current which follows the sudden application of a steady electric field and  $\tau$  is a relaxation time. The expression in Eq. (3) is known as a "stretched exponential," or as the Kohlrausch-Williams-Watts (KWW) expression for  $\phi(t)$  [3,4].

These various manifestations of broad (non-Debye) relaxation behavior have been widely discussed in the literature. The theoretical approaches are basically of two types. First, there are single-particle hopping models, involving random barriers and/or trapping sites, so that the carriers move in percolating networks [5]. Alternatively, there are the theories that regard the hopping event as involving many-particle interactions, so that the motion of a carrier is greatly influenced by the relaxation of its neighborhood, and the exponent  $s$  is a measure of the degree of interaction [6]. In both cases, there is the question of how  $s$  varies with temperature (or frequency, over a wide frequency range) and whether  $s$  can reach the limiting value,  $s=1$ . In some theories  $s=1$  is regarded as an unattainable limit [1]. In fact, for this case, there is

no decay of transient current, as given by Eq. (3). Other theories suggest that  $s$  increases toward the limit of unity as the temperature decreases [7].

The experimental situation is somewhat unclear. While for amorphous semiconductors at low temperatures, the case of  $s=1$  has been widely reported [8], the appearance of this limiting case does not seem to have been well established for ionically conducting materials. In this Letter, we examine a number of crystalline and glassy ionic conductors and show that the case of  $s=1$  is observed for some relatively simple defect systems, and also that it may appear as a limiting behavior at relatively low temperatures for systems in which, typically,  $s \neq 1$ . In this work, we are able to extend the range of temperatures downward by using an automated ac capacitance bridge (Andeen Associates CGA-83) that is capable of measuring conductances as low as  $10^{-13}$  mho over a frequency range from 10 Hz to 100 kHz in seventeen intervals. Both conductance  $G(\omega)$  and capacitance  $C(\omega)$  were measured; these measurements were then converted to  $\sigma(\omega)$  and  $\epsilon'(\omega)$  using the sample dimensions. Further details of the measurements are given elsewhere [9].

The ionically conducting materials studied, and listed in Table I, are intended to constitute a representative selection. Our objective will be to study the ac conductivity behavior in light of what is already known about  $\sigma_0$  of these materials. First, NaCl doped with divalent cations (50 ppm of Zn<sup>2+</sup>) constitutes one of the oldest and most widely studied ionic conductors, in which the charge carriers are cation vacancies that compensate for the Zn<sup>2+</sup> dopant [10]. On the other hand, Co<sup>2+</sup>-doped

TABLE I. Materials studied,  $s$  values observed, and conductivity activation energies.

Material	Temperature range (K)	$s$	$E_\sigma$ (eV)
NaCl:(50 ppm Zn <sup>2+</sup> )	298-475	1	0.95
KTaO <sub>3</sub> :(~30 ppm Co <sup>2+</sup> , H <sup>+</sup> )	430-525	1	1.01
CeO <sub>2</sub> :(6 mol% Gd <sub>2</sub> O <sub>3</sub> )	95-400	1.0-0.60	0.79
Na <sub>2</sub> O·3SiO <sub>2</sub> glass	95-400	1.0-0.60	0.72
(Na/Cs) <sub>2</sub> O·3SiO <sub>2</sub> glass	180-500	1.0-0.60	0.89

KTaO<sub>3</sub> is known to become a protonic conductor after treatment in water vapor at high temperatures [11]. Here interstitial protons compensate for the lower-valent Co<sup>2+</sup> ions that sit on Ta<sup>5+</sup> sites. Both the NaCl and KTaO<sub>3</sub> samples studied here are single crystals. The CeO<sub>2</sub> doped with 6 mol% Gd<sub>2</sub>O<sub>3</sub> is a widely studied oxygen-ion conductor [12], the carriers being oxygen-ion vacancies that compensate the Gd<sup>3+</sup> dopant which substitutes for Ce<sup>4+</sup>. This material is studied as a polycrystalline ceramic. Finally, we have made measurements on two silicate glasses, one a Na-trisilicate glass and the other a Na/Cs mixed alkali glass.

Figure 1 shows the conductance data for the NaCl sample at various temperatures. In the higher temperature range, we find  $\sigma$  independent of  $\omega$  over the low range of frequency, representing  $\sigma_0$  [see Eq. (1)]. When  $\sigma_0$  is plotted on an Arrhenius plot, a good straight-line region is obtained (covering nearly five decades in  $\sigma$ ) which gives  $E_\sigma = 0.95$  eV for the activation energy. There is no question that these results fall in the association range (stage III) of the conductivity curve, in which cation vacancies and Zn<sup>2+</sup> dopant ions are almost fully associated [10]. The corresponding migration energy for cation vacancies,  $E_m$ , is only about 0.69 eV so that  $E_\sigma$  is made up of  $E_m$  and a corresponding association energy term [13]. From the dependence of  $\sigma$  on frequency at the higher frequencies in Fig. 1, we obtain the exponent  $s$ , and find that  $s=1$  over the temperature range 298–475 K. The corresponding capacitance curves  $C(\omega)$  are essentially independent of frequency, consistent with Eq. (2) for the case  $s=1$ .

Similar behavior was found for the protonically conducting KTaO<sub>3</sub> crystal over a narrower temperature range of 430–525 K, again showing  $s=1$  behavior from

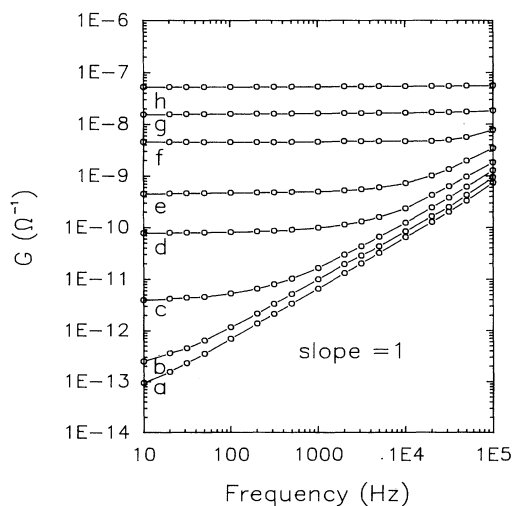


FIG. 1. Conductance as a function of frequency for NaCl:Zn<sup>2+</sup> at several temperatures. Curves a-h are at 23.0, 55.5, 90, 127.5, 156, 197.5, 226.5, and 260 °C, respectively.

the ac conductivity. Again the conductivity activation energy,  $E_\sigma = 1.01$  eV, includes an association term, since  $E_m = 0.74$  eV [14].

The oxygen-ion conducting ceramic CeO<sub>2</sub> was studied over a wide range of temperature. In the higher temperature range, 320–400 K, we have found a constant  $s=0.60$ . The conductivity activation energy  $E_\sigma$  is 0.79 eV, again higher than the migration energy of 0.61 eV [12]. Below 320 K, however,  $s$  began to rise until it reached  $s=1$  at the lowest temperatures studied, as shown in Fig. 2. Interestingly enough, the two glasses studied showed very similar behavior for their  $s(T)$  curves. The Na trisilicate data fall almost exactly on top of the data for CeO<sub>2</sub> in Fig. 2 and were, therefore, omitted from this figure; the data for the mixed alkali glass are somewhat displaced to higher temperature and are presented in Fig. 2. The relevant data for all of these materials are presented in Table I, including the conductivity activation energy  $E_\sigma$ .

For the case of a silicate glass, it has also been shown [15] that  $s=1$  behavior can be attained by going to an extremely high range of frequencies instead of to lower temperatures using a combination of techniques (IR, microwave, etc.). In such cases, however, questions might be raised about the compatibility of the various techniques. The present observation of  $s(T)$  using a single sample and a single technique is perhaps a more convincing demonstration that the limiting behavior ( $s=1$ ) occurs in all cases at the lower temperatures (but well above the cryogenic temperature region). It further suggests that  $s=1$  is *actually reached* and not just approached. Furthermore, far from requiring highly disordered systems with a wide distribution of activation energies, it is found for simple defect systems in which the defect concentrations are low, with the bound carriers present in the simple form of associated pairs. (Especially noteworthy are the cases of NaCl and KTaO<sub>3</sub>.)

Let us then consider the theoretical justification for such limiting behavior. While several models suggest

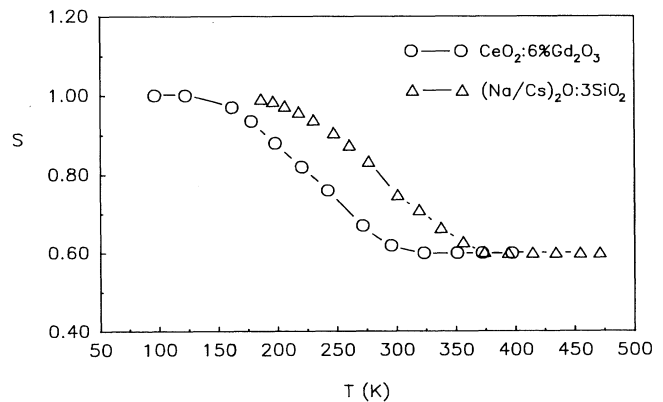


FIG. 2. Dependence of exponent  $s$  on temperature  $T$  for CeO<sub>2</sub>:Gd<sub>2</sub>O<sub>3</sub> ceramic and (Na/Cs)<sub>2</sub>O:3SiO<sub>2</sub> glasses.

that  $s(T)$  increases toward unity as the temperature decreases, there is one model that is widely quoted as giving rise to the limiting value of  $s=1$  [16]. This model considers a two-level system, involving hopping between two sites that have an energy difference [17]. For electronic carriers, the model has been considered with quantum-mechanical tunneling taking place through the barrier, but for ionic carriers at temperatures  $\sim 200$  K, only hopping *over* the barrier seems worthy of consideration. In this case, however, in order to obtain  $s=1$ , it is necessary to assume that the relaxation times vary exponentially with a parameter (e.g., an energy) that has a wide and uniform distribution of values. Such a model which is based on the existence of a high and random degree of disorder is inconsistent with the relatively simple defect structure of the three crystalline materials that we have selected. In each of these three cases, the dc conductivity is well understood in terms of the charge carriers being associated with oppositely charged defects, so that the number of free carriers is determined by a dissociation of such pairs or complexes. Thus, the model that describes  $\sigma_0$  is incompatible with the requirement of a very broad and featureless distribution function for hopping events.

In conclusion, the limiting behavior ( $s=1$ ) appears to be a universal phenomenon; yet none of the models presented in the literature offers a satisfactory explanation for this distinctive behavior.

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