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Dynamic cluster model of the ac conductivity of crystalline materials and glasses

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Many ionically conducting crystalline materials, glasses, and polymers exhibit a power-law frequency dependence of the ac conductivity with exponent $s\approx 0.6$ in the temperature range 300–500 K. To explain this phenomenon a dynamic cluster model (DCM) is suggested. DCM describes the dispersive frequency behavior and defines the range of frequency and dopant concentration at which a power-law behavior takes place. It also establishes an important role of the effective charge of carriers $Ze/\sqrt{\varepsilon_S}$. Experimental results for $Na_2O\cdot 3SiO_2$ glass and for CeO_2 and $CaTiO_3$ ceramics doped with aliovalent ions are in good agreement with this theory. [S0163-1829(98)09937-8]

I. INTRODUCTION

Many highly disordered solids, such as amorphous semiconductors, glasses, polymers and doped ionic crystals, exhibit a power-law frequency dependence of the ac conductivity over several decades in frequency. Such behavior has been observed in materials that show both electronic and ionic conductivities.[1–19] Jonscher[11] first brought attention to this behavior and referred to it as the ''universal dynamic response.'' Usually the experimental ac conductivity data can be represent as a sum of two terms as follows:

$$\sigma(\omega)=\sigma(0)+A(T)\omega^S\equiv\sigma(0)[1+(\omega\tau)^S], \qquad (1)$$

where $\sigma(0)$ is low frequency or dc conductivity, ω is the angular frequency, and s is an exponent falling in the range $0<s<1$. The temperature dependent coefficient $A(T)$ has been shown to follow an Arrhenius form with an activation energy $E_A\approx(1-s)E_\sigma$, where E_σ is the activation energy of the dc conductivity.[9,12,13] The quantity τ is an appropriate time of relaxation defined by Eq. (1), which can be written in the form:

$$\tau=\tau_0\exp(E_\tau/kt), \qquad (2)$$

with activation energy E_τ and a preexponential τ_0, that has been anticipated to equal to the reciprocal value of the characteristic phonon frequency $\nu_{ph}\approx 10^{12}-10^{13}$ Hz.[6,10] Many authors have reported that $E_\tau\approx E_\sigma$.[9,12,13] For various ionically conducting crystals and glasses several authors[9,13,16,18] have shown that at relatively high temperatures (higher than room temperature) and/or low frequencies, $s\approx 0.6$. Such behavior has been designated the ''universal dynamic response'' (UDR).[17] At lower temperatures and/or higher frequencies a different behavior is observed, in which $s\sim 1$ and the conductivity varies only weakly with temperature.[2,6,13,14,16] This behavior will not be considered here.

The earlier theories describing the disperse frequency dependence of the ac conductivity applied to electron hopping,[1,3,4,19–21] while only a few theories were devoted to the description of ionic dispersive motion.[2,22–25] The latter theories include the ''correlated barrier hopping,'' [9,22] the ''diffusion controlled'' model suggested by Elliott,[26] the ''jump relaxation'' model of Funke[10] and the ''coupling'' model of Ngai.[12] Though all of these theories predict a power-law frequency dependence of the ac conductivity, none of them appear to explain why the exponent s is close 0.6 independently of temperature and dopant concentration for a wide range ceramics and glasses. In addition, they also fail to predict the disappearance of this power-law behavior at sufficiently low dopant concentrations in experiments that we will quote in the last section of the present paper. In this paper we propose a new model, called the ''dynamic cluster model'' (DCM), which describes dispersive frequency behavior in terms of a system consisting of randomly distributed inclusions of relatively high conductivity (region ''1'') imbedded in a matrix of lower conductivity (region ''2''). This model is based on an analysis originally suggested by Efros and Shklovskii[27] for description of a binary system consisting of randomly distributed metallic inclusions in a dielectric matrix in the presence of a low frequency electric field.

II. DYNAMIC CLUSTER MODEL

The model of Efros and Shklovskii[27] cannot be directly applied to describe experimental results in ionically conducting doped crystalline ceramics and glasses because there are no metallic inclusions in these materials. However this percolation model can be generalized to involve clusters of more highly conducting regions ''1'' surrounded by weakly conducting regions ''2.'' (For simplicity we assume just two type regions in this model.) We assume that, due to Coulomb potential fluctuations created by the charges randomly distributed in the sample, the local height of the potential barrier near some carriers might be lowered. As these carriers begin to move under an applied field, they implicate other carriers through interactions. Due to Brownian motion of carriers located near the locally decreased potential barriers, these carriers are displaced by the diffusion length $\propto(D_1/\omega)^{1/2}$ during half of a period of the alternating electric field, π/ω (where D_1 is the diffusion coefficient in the highly conducting region, with corresponding activation energy E_1). These carriers occupy regions which can be presented roughly as spheres of radius R_1:

$$R_1\sim(6\pi D_1/\omega)^{1/2}\equiv[6\pi kT\sigma_1/n(Ze)^2\omega]^{1/2}, \qquad (3)$$

where (Ze) is the charge of moving particle, n is the carrier concentration in the sample, while the diffusivity D_1 is replaced by the conductivity σ_1 by applying the Nernst-Einstein relation. (We neglect the direct carrier motion under electric field because the energy obtained by carriers from electric field is small compared with kT.[28]) The frequency of the alternating field determines only a mean cluster size. For the rest of the sample (weakly conducting regions) we set the activation energy equal to E_2 which may be regarded as higher than E_1 by an energy gap $\Delta \equiv E_2 - E_1$. Thus, in our model we assume that highly conducting clusters appear due to Brownian motion of carriers randomly distributed in space. If one assumes that $(\Delta/kT) \gg 1$, then the dc conductivity, σ_1, in the highly conducting phase is much higher than the conductivity σ_2 in the weakly conducting region. With a decrease in the applied field frequency, the volumes of the highly conducting clusters increase, until they overlap at a frequency ω_C and percolation occurs. We will presume also that, due to high mobility of carriers, the dc conductivity contribution is always much higher than the polarization contribution in the highly conducting regions ($\sigma_1 \gg \omega\varepsilon_S/4\pi$), where ε_S is the static dielectric constant, which, for the simplicity, is regarded to be the same for both regions. In the weakly conducting regions (''2'') the mobility of carriers is very low, and we will describe the corresponding complex conductivity, $\sigma_2^* = \sigma_2 - (i\omega\varepsilon_S/4\pi)$, as sum of a dc conductivity, σ_2, and a polarization term, $-(i\omega\varepsilon_S/4\pi)$. These two contributions compete: at very low frequency the σ_2 contribution prevails, while at high frequencies ($\omega \gg 4\pi\sigma_2/\varepsilon_S$) the polarization term is more important. To find the characteristic frequency ω_C we used the model of overlapped spheres[30] for the continuum problem in 3D space, which is found to be most convenient for description of conductivity in disordered systems. Here the critical volume fraction at the percolation threshold, v_C, was determined to be equal to ~1/3. Combining Eq. (3) with the expression $4\pi(R_C/2)^3 n/3 \approx 2.7/8 \approx v_C$ given by Pike and Seager for the percolation radius[30] and taking into account that $\sigma_1 \gg \omega\varepsilon_S/4\pi$, one can obtain the frequency ω_C as follows:

$$\omega_C \approx \pi(kT/W)\tau_1^{-1} < \tau_1^{-1}, \tag{4}$$

where $W = (Ze)^2/\varepsilon_S r_0$ is the Coulomb repulsive energy between carriers, $\tau_1 = (\varepsilon_S/4\pi\sigma_1)$ is the Maxwell relaxation time in the conducting region and $r_0 = (4\pi n/3)^{-1/3}$ is the average distance between carriers.[31] It will be assumed that, with a further decrease in the frequency ($\omega < \omega_C$) the volume of highly conducting regions practically will not change.[32] Thus, we suppose that at frequencies lower than ω_C the volume fraction of the highly conducting regions would be practically constant and equal to v_C.

To extend the model of Efros and Shklovskii[27] to ionic systems with low dopant content we will start from a more general assumption, keeping in mind that diffusivity and conductivity of amorphous materials or of crystalline materials with cubic symmetry are scalar. Let us write the effective complex conductivity, σ^*, of a binary system consisting of randomly distributed inclusions with conductivity σ_1 in a matrix with complex conductivity σ_2^* in the scaling form:[27,29] $\sigma^* = \sigma_1 f(v,z)$, where $z \equiv \sigma_2^*/\sigma_1$, and $|z| \ll 1$. Since the effective conductivity of such system is invariant to the replacement σ_1 by σ_2 and, simultaneously, v by $(1-v)$, the $f(v,z)$—function must satisfy the relation[29]

$$f(v,z) = z f(1-v, z^{-1}). \tag{5}$$

One can find a general solution of Eq. (5) in the form $f(v,z) = \alpha_1 z^{1-v} + \alpha_2 z^v$. Taking into account the condition that $\sigma = \sigma_2$ when $v = 0$, one finds $\sigma^* = \sigma_1 z^{(1-v)}$. As mentioned above, at the frequency $\omega < \omega_C$ the fractional volume of the high conducing regions $v \approx \text{constant} \approx v_C$. Thus, in this frequency range we obtain

$$\sigma^* = \sigma_1 z^{(1-v_C)}. \tag{6}$$

Consequently, when the polarization contribution in σ_2^* is much higher than the conductivity σ_2, the real part of the effective conductivity, σ, can be written as

$$\sigma = \sigma_1(\omega\varepsilon_S/4\pi\sigma_1)^{(1-v_C)}\sin(\pi \cdot v_C/2). \tag{7}$$

Because of the assumption that $(\omega\varepsilon_S/4\pi) > \sigma_2$, there exists a range of ω such that Eq. (7) is obeyed:

$$(4\pi\sigma_2/\varepsilon_S) \equiv \tau_2^{-1} < \omega < \omega_C. \tag{8}$$

Here τ_2 is the Maxwell relaxation time in the weakly conducting region. In this frequency range one can rewrite Eq. (7) as follows:

$$\sigma \propto \sigma_1^{v_C}\omega^{(1-v_C)} \propto \exp(-v_C E_1/kT),$$

$$\sigma_i = [n(Ze)^2 \nu_0 \lambda^2/kT]\exp(-E_i/kT), \tag{9}$$

where λ is the lattice parameter, ν_0 is the vibration frequency, $i = 1, 2$. In the case of high enough frequencies when the first term in Eq. (1) might be neglected, comparing Eqs. (1) and (9) shows that

$$E_A = v_C E_1, \tag{10}$$

where $v_C \equiv 1 - s$. Thus, the activation energy E_A has a meaning of the energy activation of carriers in the highly conducting region averaged over the entire sample.

On the other hand, in the low frequency limit, $\omega \ll (4\pi\sigma_2/\varepsilon_S) \equiv \tau_2^{-1}$, one finds a low frequency or dc conductivity, $\sigma(0)$, as follows:

$$\sigma(0) = \sigma_1^{v_C}\sigma_2^{(1-v_C)} \propto \exp(-E_\sigma/kT), \tag{11}$$

where

$$E_\sigma = v_C E_1 + (1-v_C)E_2 \equiv E_1 + (1-v_C)\Delta, \tag{12}$$

so that the activation energy E_σ has a meaning of the average activation energy per particle in both regions. Combining Eqs. (7) and (9) one obtains an approximation for the effective ac conductivity in the form of Eq. (1) which is valid in both low and high frequency limits, with $s = 1 - v_C$.

The time of relaxation τ of Eq. (1) has the form

$$\tau^{-1} = \tau_2^{-1}[\sin(\pi v_C/2)]^{-1/(1-v_C)} \equiv (A_\tau/T)\exp(-E_2/kT) \propto \exp(-E_\tau/kT). \tag{13}$$

This quantity has a meaning the relaxation time in weakly conducting region and its preexponential differs from that given in Eq. (2). Consequently the activation energy $E_\tau = E_2$ has a meaning of the activation energy of carriers in the poorly conducting region. In 3D space $v_C \sim 1/3$, consequently $s \approx 2/3$, which is close to Efros and Shklovskii's result.[27] Using Eq. (10) and keeping in mind that $E_\sigma \approx E_1 \approx E_2$ since $\Delta \ll E_1$ one obtains the activation energy E_A as follows: $E_A = (1-s)E_1 \approx (1-s)E_\sigma$.

The approach developed in the present paper also allows us to find the concentration threshold (the minimal level of carrier concentration) at which the dynamic universal regime (UDR) may be observed. Combining Eqs. (4) and (8) we have $\omega < \pi(kT/W)\cdot\tau_1^{-1} < \tau_1^{-1}$. Evidently this inequality is valid under the condition

$$kT/W \ll 1. \tag{14}$$

(A similar result was obtained by Maas *et al.*[31] from computer simulation in the lattice gas model.) By setting $kT/W = 1$ one can find the minimal level of carrier concentration, n^*, at which the the UDR occurs, as follows:

$$n^* \sim [\varepsilon_S kT/(Ze)^2]^3 = r_{\mathrm{On}}^{-3}. \tag{15}$$

From the equality (15) it is seen that if the mean distance between charges $r \sim n^{-1/3}$ is less than the ''Onsager radius'' $r_{\mathrm{On}} = (Ze)^2/\varepsilon_S kT$, these carriers ''feel'' each other and the UDR takes place. In the opposite case, charged particles do not feel each other and UDR disappears. Equation (15) also predicts that materials with a small dielectric constant, or more exactly, materials with greater effective charge of carriers $Ze/\sqrt{\varepsilon_S}$ are more suitable for manifestation of the frequency power-law conductivity behavior (UDR). In other words, from Eq. (15) it follows that at a given temperature, materials with a small permittivity can exhibit the UDR phenomenon at low enough carrier concentration, while materials with a higher permittivity cannot. With a decrease in temperature this power-law phenomenon can also hold for materials with higher dielectric constant at low carrier concentration, however, the frequency window may be very narrow for the experimental observation of the UDR [see Eq. (8)].

III. COMPARISON WITH EXPERIMENTAL RESULTS AND CONCLUDING REMARKS

(1) The approach developed in the present paper predicts a power-law frequency dependence with the exponent $s = 1 - v_C \approx 2/3$. Experimental values of s in the range 0.6–0.7 are typically found for many systems. Figure 1 illustrates this by showing that the reduced conductivity $[\sigma - \sigma(0)]/\sigma(0)$ for 12% Y^{3+}-doped CeO_2 ceramics, $Na_2O\cdot 3SiO_2$ glasses and 30% Al^{3+}:$CaTiO_3$ ceramics plotted versus $\omega\tau$ in log-log scale yields a master curve with slope $s \approx 0.6-0.64$ in each case. Other examples yielding such s values include Y^{3+} and Gd^{3+} doped (1 to 12%) cerium oxide ceramics,[15] 15% Al^{3+}:$CaTiO_3$ ceramics,[13,17] $(Ag_2SO_4)_{0.3}\cdot(AgPO_3)_{0.7}$,[18] and $x Li_2O\cdot(1-x)GeO_2$ ($x = 5-35$ mol%)[33] glasses.

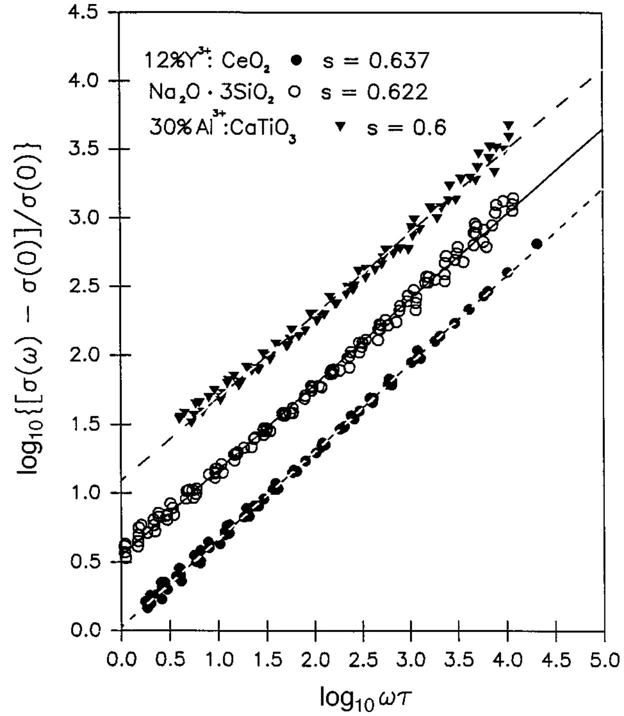

FIG. 1. The master curves of the normalized ac conductivity $\{[\sigma(\omega) - \sigma(0)]/\sigma(0)\}$ vs $\omega\tau$ for three materials in a log-log plot. The curves are shifted for clarity.

(2) Using Eq. (15), we found the lowest level of carrier concentration for UDR power-law behavior in doped cerium oxide ceramics at 400 K to be $n^* \approx 0.006\%$, representing the oxygen vacancy concentration. (Recall that the impurity concentration is twice this value.) This is consistent with the fact that UDR behavior is still observed for 1% Y^{3+} or Gd^{3+} doping and only disappears for a nominally pure or ''undoped'' CeO_2 sample.[15]

(3) The theory predicts an important role of the carrier effective charge $Ze/\sqrt{\varepsilon_S}$. Thus, for materials with high dielectric constant, n^* is predicted to be much higher than for a material such as ceria (at the same temperature). This conclusion is supported by results for Al^{3+}-doped $CaTiO_3$, where it was shown[13] that, for 15% and 30% Al^{3+} at 500 K a power law behavior with $s \approx 0.6$ is observed, while for 1.5% and 5% Al^{3+} doped $CaTiO_3$ ceramics it was found that $s \approx 0.85$,[13] which falls out of the UDR range. In the case of higher dopant concentrations $\varepsilon_S \sim 65$ and Eq. (15) gives $n^* \sim 1\%$, while in this case of two lower concentrations $\varepsilon_S \sim 130$ and $n^* \sim 8\%$.

(4) For most doped ceramics discussed in this paper as well as for glasses E_τ is a little more than E_σ. This result follows from Eq. (12), because $E_\sigma = E_\tau - v_C\Delta$, and the second term is ~0.03 eV, in good agreement with experimental results.

(5) A surprising result in our analysis is also that τ_0^{-1} [see Eq. (2)] is 2–3 orders of magnitude higher than we could expect for characteristic phonon frequency. Since τ_0^{-1} cannot be regarded as attempt frequency, it follows that τ^{-1} is not a hopping frequency, as Almond and West[34] have claimed. However, as was shown above, the quantity τ in Eq. (1)

should be determined by Eq. (13). With the aid of Eqs. (9), (13), and Ref. 35 one can find for dilute solution cerium oxide ceramics $A_\tau \sim 10^{17}$ sec^{-1} K in good agreement with fitting for 1% Y^{3+}-doped CeO_2 ceramics. Thus, it is apparent that the quantity τ has a meaning of the Maxwell relaxation time in a weakly conducting region.

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