Electrical relaxations: Simple versus complex ionic systems

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Complex materials are known to show two regions of ac electrical behavior. In the high-temperature/low-frequency domain, they show power-law frequency dependence of the conductivity known as ''universal dielectric response,'' or UDR, while at low temperatures/high frequencies they show ''nearly constant loss,'' or NCL behavior, which persists down to cryogenic temperatures. The present paper seeks to examine the corresponding behaviors of ''simple'' systems, i.e., dilute systems of the classical type in which a relatively small number of defects are involved. Three systems studied here are oxygen-ion conductors: CeO_2 doped with Gd^{3+} and with Y^{3+}, as well as $CaTiO_3$ doped with Al^{3+}. In each case, we proceed from dilute to concentrated doping levels. Also studied in very dilute concentrations are $NaCl:Sm^{3+}$ (a Na^+ conductor) and $KTaO_3:Cu^{2+},H^+$ (a protonic conductor). It is found that in the UDR regime, the simple materials show very much the same behavior as the complex, suggesting that UDR relaxation is intrinsic to the hopping process. A striking result is that the onset frequency of dispersive conductivity corresponds to the mean jump frequency of all carriers, both bound and free. In contrast to the UDR regime, NCL behavior is only shown by complex materials; simple materials show discrete (Debye-type) relaxations that are due to off-center configurations that relax by small rocking-type motions. As the concentrations increase, these relaxations smear out into a broad distribution that gives rise to NCL behavior.

I. INTRODUCTION

The electrical behavior of complex ionically conducting materials (e.g., glasses, highly doped crystals, and polymers) as a function of frequency shows surprising simplicities involving two regions of behavior. Specifically, at relatively high temperatures and/or low frequencies, a power-law behavior of the conductivity σ is observed of the form

$$\sigma(\omega) = \sigma(0)[1 + (\omega\tau)^s], \qquad (1)$$

where $\sigma(0)$ is termed the ''dc conductivity,'' ω is the angular frequency, and the exponent s falls in the range from 0.5 to 0.7. Such behavior was given notoriety by Jonscher, who termed it ''universal dielectric response,'' or UDR.[1,2] This power-law behavior, which is observable for several decades in frequency (although it obviously cannot continue to be valid at the limiting values of frequency), is a result of defect interactions in the ion hopping process. A wide range of theories for UDR behavior has been proposed.[3–9]

The second type of behavior occurs at low temperatures and/or high frequencies, and shows $\sigma(\omega)$ as very close to a first-power law in frequency, and in addition, only very slowly temperature dependent.[10–17] Since this behavior persists down to cryogenic temperatures, it is clearly a dielectric phenomenon rather than a conductive one, and therefore more conveniently described in terms of the complex dielectric constant ε^*. In particular, the imaginary part of ε^*, i.e., ε'', which measures the energy loss per cycle, is related to the conductivity by

$$\varepsilon''(\omega) = \sigma(\omega)/\varepsilon_0\omega, \qquad (2)$$

where ε_0 is the vacuum permittivity. Accordingly, a first-power dependence of σ on ω means a constant ε'', so that this region has been termed ''nearly constant loss,'' or NCL.[18]

These behaviors for complex systems have been widely discussed. In fact, a series of conferences have been held under the title ''Relaxation in Complex Systems.''[19] But traditionally, defect studies in ionic crystals have been carried out for ''simple'' systems, notably crystals doped with dilute concentrations of aliovalent impurities, so as to produce a relatively small number of discrete defects whose interactions can be studied. Such studies are covered in numerous textbooks and review articles.[20–23] Let us mention a couple of examples of simple systems. Probably the most widely studied system is that of NaCl crystals doped with divalent impurities D^{2+} and giving rise to the defects: $D_{Na}^{\cdot} + V_{Na}'$ (in Kroger-Vink notation). Another is CeO_2 (which has the fluorite structure) doped with trivalent cations M^{3+} so as to produce defects: $2M_{Ce}' + V_O^{\cdot\cdot}$. In both of these dilute systems, the defect structures are well understood, including the role of the respective vacancies in the conduction process and the interaction of the charged defects to produce associated clusters.

Surprisingly, there has been almost nothing published on the question of how simple systems behave in the UDR and NCL regimes, or in general, on what constitutes the transition from simple to complex systems. In this paper, we look into these questions by examining some crystalline systems that can be taken from the dilute into the concentrated defect range (i.e., from simple to complex), as well as others that allow only very dilute doping. It is felt that since defects in simple systems are well understood, such a study can contribute to a better understanding of the UDR and NCL phe-

nomena in general. The next two sections will deal separately with the UDR and NCL phenomena.

II. THE UDR REGIME

A. Background

There are two key parameters in Eq. (1), viz., the dc conductivity $\sigma(0)$ and τ. Clearly, τ^{-1} is the frequency at which $\sigma(\omega)=2\sigma(0)$. We find it more convenient to define an *onset frequency* (the beginning of dispersion) ω_{on} as that at which $\sigma(\omega)=1.58\sigma(0)$ (i.e., where the logarithmic increase in σ is 0.2). Thus, $\omega_{on}\approx0.4\tau^{-1}$ depending slightly on the value of the exponent s.

The expression for the dc conductivity $\sigma(0)$ is well known[21] and may be written as

$$\sigma(0)T=q_i^2\lambda_i^2 c_i\Gamma_i/6kv_M, \qquad (3)$$

where k is Boltzmann's constant, v_M is the molecular volume, and the remaining quantities are the properties of the ionic carriers: c_i, their mole fraction; λ_i, the jump distance; q_i, the effective charge; and Γ_i, their jump frequency. (In this equation we omit the ''conductivity correlation factor'' as being unimportant.)

It is well known that there are two important limiting cases for crystals with dilute defects.[21] The first is the ''extrinsic dissociated region,'' often called stage II, in which almost all the carriers are dissociated and therefore available for conduction. In this case, $c_i=c_0$, where c_0 is the entire defect concentration as determined by the aliovalent doping. Thus, for stage II, we have

$$E'_\sigma=E_m \quad \text{(stage II)}, \qquad (4)$$

where E'_σ is the Arrhenius activation energy of $\sigma(0)T$ (following the notation of a previous paper[24]), and E_m that of the jump frequency Γ_i. The second region, occurring at lower temperatures, is the ''extrinsic associated region,'' called stage III, in which most of the carriers are associated with dopants, so that $c_i\ll c_0$ and varies as $\exp(-rE_a/kT)$, where E_a is the association energy and r is a simple numerical factor (usually $\frac{1}{2}$ or 1, depending on the charge of the dopant[21]). Thus in this case,

$$E'_\sigma=E_m+rE_a \quad \text{(stage III)}, \qquad (5)$$

An important observation in UDR behavior is that ω_{on} (or τ^{-1}) is consistently found to have an activation energy E_{on} equal to E'_σ.[18,24–26] In fact Almond and co-workers[27,28] have suggested that τ^{-1} is the hopping frequency Γ_i of the carrier defects. This claim would imply, as a consequence of Eqs. (4) and (5), that E_{on} would only equal E'_σ in the case of stage II behavior, but not in the case of strong association (stage III). However, observations on CeO_2 doped with Y^{3+} and Gd^{3+} show that this equality is still valid in the stage III region.[24]

In order to interpret this result, we now suggest that ω_{on} is related to the mean jump frequency Γ_{av} of all carriers, both bound and free. For stage II, this is the same as Γ_i but for stage III, this is a substantially lower frequency, specifically
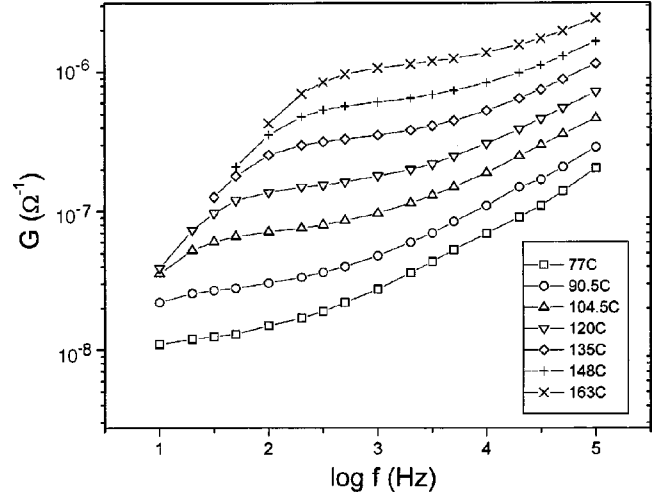

FIG. 1. Variation of conductance G with frequency f for CeO_2:1%Gd at various temperatures. (For the higher temperatures, points at low frequencies have been omitted for clarity.)

$$\Gamma_{av}=(c_i/c_0)\Gamma_i, \qquad (6)$$

i.e., the product of the probability of a carrier being free and the jump frequency of free carriers. Then clearly, Γ_{av} has the activation energy given by Eq. (5), and the final expression for $\sigma(0)$ may be written as

$$\sigma(0)T=(q_i^2\lambda_i^2/6kv_M)c_0\Gamma_{av}, \qquad (7)$$

which is valid for both stage II and stage III. This expression allows us easily to calculate Γ_{av} from $\sigma(0)$ so long as c_0 is known from the doping level. A key objective in this paper will be to numerically relate ω_{on} to Γ_{av}.

B. Results and discussion

We will first examine three systems in which the dopant concentration is varied from the dilute (1–2%) to the concentrated (>10%) range. The dilute samples may reasonably be regarded as ''simple'' systems, since the probability of a dopant having another dopant atom as the nearest or next-nearest neighbor is not high. A further indication is that, when a relaxation loss peak due to the reorientation of bound pairs is observed in dilute samples, such a peak is found to be very close to a Debye peak indicating the absence of significant interactions.[21]

The measurements of conductance $G(\omega)$ and capacitance $C(\omega)$ are made in an automated ac bridge over the frequency range $10-10^5$ Hz in 17 intervals. These data are then converted, with appropriate geometric factors, into $\sigma(\omega)$ in $(\Omega\,cm)^{-1}$ and relative dielectric permeability, $\varepsilon'(\omega)$, respectively. Further information about both sample preparation and measurements has been given elsewhere.[24]

We begin with CeO_2 doped with Gd^{3+} and with Y^{3+}. Figure 1 shows data for $G(\omega)$ vs frequency in an appropriate temperature range for a 1% Gd-doped sample. (In this figure, and throughout this paper, ''log'' represents $\log_{10}$.) It should be noted that the curves show three ranges of behavior. First,
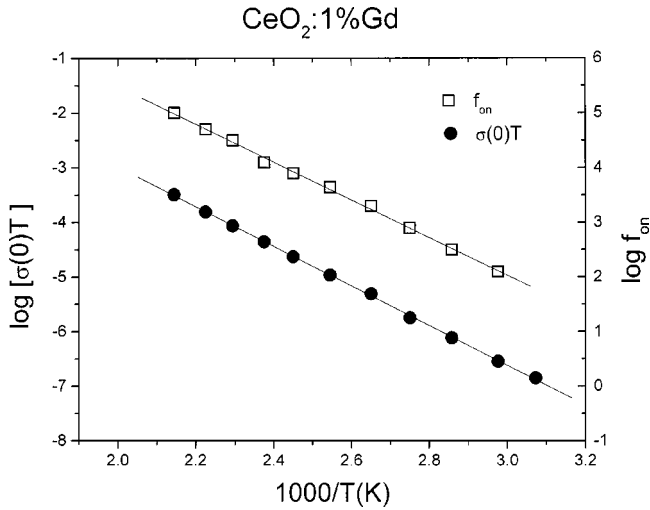
FIG. 2. Arrhenius plots of the product of dc conductivity and T, and of the onset frequency f_{on} for CeO$_2$:1%Gd.

for the higher temperatures, there is a strong rise at low frequencies. This is the grain-boundary blocking effect, which has been studied in detail earlier;[29] it is not present for single crystals or for glasses. Second, there is a near-plateau range, representing the "dc conductivity" $\sigma(0)$. Finally there is the higher frequency climb, which is the (UDR) conductivity relaxation in which we are primarily interested. Because of the grain-boundary effect, the dc region is not flat. Thus, in analyzing these data, we obtain $G(0)$ and correspondingly $\sigma(0)$ from a complex-impedance plot, using the intersection of the first arc with the real axis in the usual way.[30] The restriction of having a limited frequency window can be partially overcome by varying the temperature; thus in Fig. 1 we see that, as temperature increases, the pattern of the $G(\omega)$ curve moves toward higher frequencies as well as to higher G values. Accordingly, at high temperatures, the UDR region disappears from our frequency "window," while at low temperatures, the grain-boundary effect leaves the "window."

From such data, we may obtain the UDR onset frequency $f_{on}(=\omega_{on}/2\pi)$ as a function of temperature. Figure 2 shows these results obtained from the data of Fig. 1 in an Arrhenius plot, together with the Arrhenius plot of the dc conductivity [$\log \sigma(0)T$ vs $1/T$]. The corresponding activation energies are quite close, here giving $E_{on}=0.70$ eV and $E'_{\sigma}=0.72$ eV, respectively. We also obtain ω_0, the preexponential of the onset frequency defined by

$$\omega_{on}=\omega_0 \exp(-E_{on}/kT), \qquad (8)$$

which, in this case, turns out to be $\omega_0=10^{13.3}$ sec^{-1}.

With the aid of Eq. (7), we may calculate Γ_{av} at a reference temperature and compare it to ω_{on} at that same temperature. In this calculation, we have taken q_i equal to twice the electronic charge and λ_i as half the lattice parameter. In this way, we find that at $T=436$ K, $\Gamma_{av}=7.6\times10^5$ sec^{-1}, while $\omega_{on}=2\times10^5$ sec^{-1}, so that the ratio $\omega_{on}/\Gamma_{av}=0.26$.

TABLE I. Principal results obtained from the ac conductivity data of the various samples studied.

Material	E'_σ (eV)	E_{on} (eV)	$\log \omega_0$ (sec^{-1})	ω_{on}/Γ_{av}
CeO$_2$:Gd^{3+}				
1%	0.72	0.70	13.3	0.26
2%	0.71	0.73	14.3	0.4
11.3%	0.79	0.80	15.5	3.0
CeO$_2$:Y^{3+}				
1%	0.84	0.85	14.3	0.3
2%	0.81	0.83	14.6	0.7
4%	0.80	0.82	14.8	2.0
7.7%	0.88	0.90	15.6	0.7
11.4%	0.88	0.89	15.1	2.6
CaTiO$_3$:Al^{3+}				
1.5%	0.95	0.96	15.9	6.0
15%	1.14	1.12	14.8	0.9
30%	1.22	1.27	15.8	3.0
NaCl:Sm^{3+}	0.99	0.94	15.7	2.5
KTaO$_3$:Cu^{2+}H$^+$	1.03	1.09	15.8	

(Since the two activation energies are so close, the choice of the reference temperature will hardly affect the ratio obtained.)

The final parameter of interest is the power-law exponent s, which is obtained from a plot of $\log[G(\omega)-G(0)]$ vs $\log \omega$ at any temperature, or even better, from a master plot of $\log[G(\omega)-G(0)]/G(0)$ vs $\log(\omega/\omega_{on})$ for several temperatures. As reported previously, the value of s obtained in this way is close to 0.6 for the 1% Gd sample.[24]

For CeO$_2$:Gd^{3+}, we have also studied the compositions with 2% and 11.3% Gd in a similar way. The results are summarized in Table I. It is clear that the electrical behavior is very similar for both the dilute and concentrated samples.

For the second series, we turn to the system CeO$_2$:Y^{3+}, in which five compositions: 1%, 2%, 4%, 8%, and 11.3% Y, have been studied. The results are similar to those for Gd doping and are summarized in Table I.

The third system studied is CaTiO$_3$ doped with Al^{3+}. This is also an oxygen-ion conductor that posesses the perovskite structure and has defects, $2Al'_{Ti}+V_0^{\cdot\cdot}$. Measurements were carried out on a dilute 1.5% Al sample, as well as on samples with a high dopant concentration: 15% and 30% Al. Again the results are presented in Table I.

One difference between this system and the dilute ceria systems is that for the CaTiO$_3$:1.5% Al sample, the exponent s is not temperature independent. This question can be examined with the aid of Fig. 3, which shows the "apparent" s value, obtained from the slope of the plot of $\log[\sigma(\omega)-\sigma(0)]$ vs $\log \omega$ as a function of temperature for the dilute 1.5% as well as the concentrated 30% samples. The 30% sample shows the usual behavior, where the low-temperature plateau is the NCL regime, the high-temperature plateau is the UDR regime, while the intermediate regime, where the apparent s drops steeply, is where both processes are operating simultaneously.[31] In contrast, the data for the 1.5% sample show that the purely UDR regime is just reached
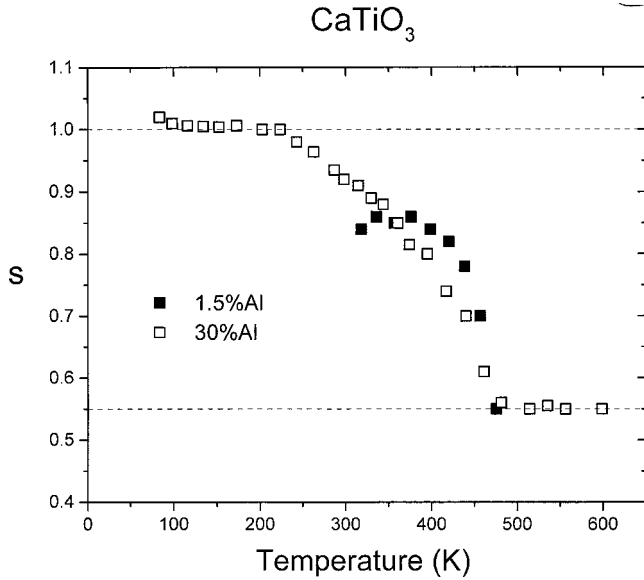
FIG. 3. Comparison of dependence of ''apparent'' power-law exponent s on temperature for $CaTiO_3$:30%Al with data for $CaTiO_3$:1.5%Al.

FIG. 4. Schematic diagram of an asymmetric double-well potential barrier with barrier height V and asymmetry energy Δ.

when the measurements cut off. This behavior can be explained by the lower activation energy E_{on} for the 1.5% sample (0.96 eV vs 1.2 eV for the 30% sample) The reason is that for the present apparatus, the cutoff occurs when $\omega_{on} \sim 10^5$ sec^{-1}; thus from Eq. (8), the cutoff temperature should be proportional to E_{on}. In spite of this early cutoff, the results for the 1.5% sample show that the value of the onset frequency ω_{on} can be reliably obtained, even when measured at the start of the intermediate regime. This occurs because the onset is defined to be at a relatively low frequency where UDR behavior is dominant, i.e., before any contribution from NCL has set in.

It is clear that for all three of these systems, the behavior of the dilute samples is closely analogous to that of the concentrated samples except that, in the dilute samples, the power-law behavior may not cover as large a frequency range as in the concentrated samples. A major reason for this fact is the presence of discrete relaxations due to reorientation of paired defects in dilute samples.[24]

In summary, the common features of the data for both dilute and concentrated samples are the following: (a) in all cases E_{on} is close to E'_σ, (b) the preexponential ω_0 is generally rather high ($\sim 10^{14}$–10^{15} sec^{-1}), and (c) the ratio $\omega_{on}/\Gamma_{av} \sim 1$, to within an order of magnitude.[32] This last result is also completely consistent with the scaling law suggested by Roling et al.,[33] whereby a plot of $\sigma(\omega)/\sigma(0)$ as a function of $\omega c_0/\sigma(0)T$ (in our notation) gives a master curve covering a moderate range of temperatures and composions of a family of glasses.[34] However, the conclusion by these authors that such results are confined to materials behaving as ''strong electrolytes'' (i.e., stage II behavior) is not justified in the light of present considerations.

Finally, we turn to two ''very dilute'' systems with defect concentrations as low as $\sim 0.01\%$, namely, NaCl:Sm^{3+}, which conducts by the movement of sodium-ion vacancies,
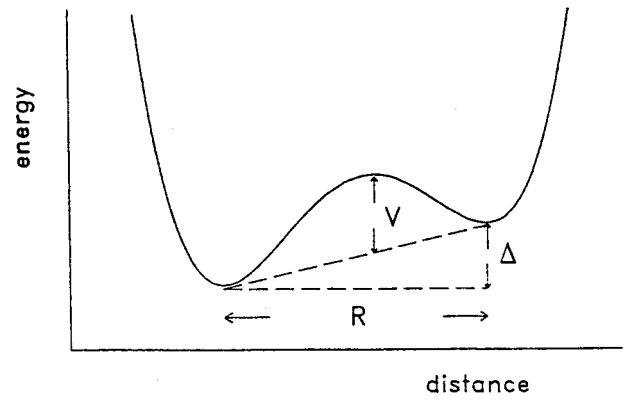
and KTaO$_3$:Cu^{2+}, which, following high-temperature treatment in water vapor, absorbs hydrogen and becomes a proton conductor.[35] The results for these two systems, which are included in Table I, show a remarkable similarity to those of the dilute and concentrated systems studied earlier, in the near equality of E'_σ and E_{on}, and in the fact that the ratio ω_{on}/Γ_{av} is close to unity in the case of NaCl:Sm. (For KTaO$_3$:Al there is a large uncertainty in this ratio due to the fact that the defect concentration c_0, and consequently Γ_{av}, is not well determined.) In these very dilute cases, as in the case of $CaTiO_3$:1.5%Al, the values of the power-law exponent s are somewhat ambiguous; however, this does not interfere with the equality of E'_σ and E_{on} and with the relationship between ω_{on} and Γ_{av}.

In conclusion, the occurrence of the same principal features of UDR for both dilute (''simple'') and concentrated (''complex'') systems means that UDR behavior is intrinsic to the process of ionic conduction. The key characteristic, mentioned above, is that $\omega_{on} \sim \Gamma_{av}$. This result, along with equality of the corresponding activation energies ($E_{on} = E'_\sigma$) means that successful hopping requires a relaxation of the surrounding ionic environment (including both free and bound ions) as an inherent part of the hopping process. This concept is particularly well exemplified by the jump-relaxation model of Funke.[5] The only puzzling result is that the onset preexponential ω_0 is generally rather high ($\sim 10^{14}$–10^{15} sec^{-1}). This may be due to a positive entropy of association, as well as that of activation, since association is also involved in the systems that we have studied.

III. THE NCL REGIME

A. Background

The principal characteristics of the NCL regime are that ε'', or tan $\delta (= \varepsilon''/\varepsilon')$ is nearly independent of frequency, as well as only very slowly temperature dependent. Since this regime extends down to cryogenic temperatures, it must involve a dielectric-relaxation phenomenon, rather than one associated with defect hopping. The accepted explanation for NCL behavior is that it arises from a superposition of asymmetric double-well potentials (ADWP's), of the type shown in Fig. 4, with a broad distribution of both the barrier heights
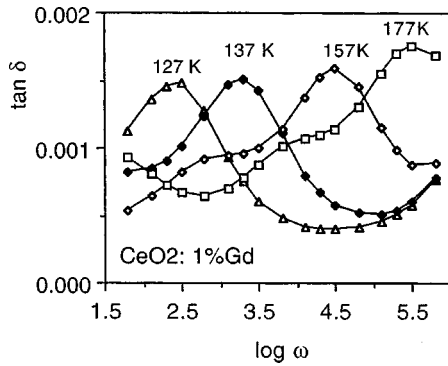
FIG. 5. Dielectric loss tan δ as a function of angular frequency ω for CeO$_2$:1%Gd at four different temperatures.

FIG. 6. Comparison of tan $\delta(\omega)$ plots for CeO$_2$ with 1%, 2%, and 11.3% Gd, all measured at 147 ± 1 K.

V and the asymmetry energies Δ.[36,37,16] But such a model provides only a phenomenological description, leaving open the question: what are the origins of this wide distribution of ADWP's? Since such low activation-energy barriers can more readily be imagined for complex than for simple systems, it becomes especially important to investigate the NCL regime for a number of dilute materials.

B. Results and discussion

In examining NCL behavior, we again turn to the three systems that have been studied in the previous section: CeO$_2$:Gd^{3+}, CeO$_2$:Y^{3+}, and CaTiO$_3$:Al^{3+} with both dilute and concentrated samples in each case. The key characteristics of the NCL behavior that we have observed for these systems may be summarized as follows.

(1) For the concentrated samples, measurements in the temperature range 55–100 K show that the loss factor tan $\delta(=\varepsilon''/\varepsilon')$ is nearly constant with frequency. Most often, it will increase slightly, typically by ~ 1.2 over the frequency range of measurement (corresponding to a conductivity power-law exponent of 1.02). The dilute samples, however, do not show this characteristic result but are more inconsistent, with tan δ often decreasing with increasing frequency.

(2) The values of tan δ for different samples of the same composition may vary by as much as a factor of 2, even for the concentrated samples.

(3) Results at ~ 4 K are only slightly smaller (typically by $\sim 30\%$) than those at 55 K.

(4) The most striking difference between the dilute and concentrated samples is that, while the latter continue to show only a gradual increase with temperature, each of the dilute samples shows one or more discrete relaxation peaks as the temperature is increased. Figure 5 shows a double peak as a function of frequency for the case of CeO$_2$:1%Gd at four different temperatures.

The two ''very dilute'' materials were also examined in the low-temperature region. The NaCl:Sm^{3+} sample showed extremely low values of tan δ, which may have been the instrumental background; the KTaO$_3$:Cu^{2+} gave larger values, but they strongly increased with increasing frequency. Thus, these samples do not show conventional NCL behavior.

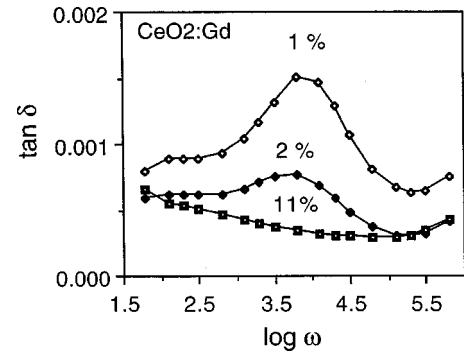The most striking observation is the appearance of discrete peaks for the the dilute CeO$_2$ and CaTiO$_3$ samples. Accordingly, the remainder of this section will be focused on these discrete peaks, their characteristics, and their implications.

Examination of Fig. 5 shows, first, that the main peak is virtually a Debye peak, but also that there exists a smaller auxiliary peak at lower frequencies. An Arrhenius plot of the peak frequencies as a function of temperature gives an activation energy of 0.28 eV for the main peak for CeO$_2$:Gd^{3+}. Figure 6 shows how this peak changes as the concentration is increased; we see that the peak is smaller for the 2% sample and that it disappears for the 11.3% sample. It is very significant that for a 2% sample, which may still be regarded as dilute and contains twice as many defects as the 1% sample, the peak height should be substantially decreased.

Similar results are obtained for CeO$_2$:Y^{3+}. In this case, the peak appears at a lower temperature and has a lower activation energy than that for the Gd-doped samples. Again, an auxiliary peak is seen at lower frequencies, and going from a 1% to a 2% sample results in a decrease of the main peak. Finally, for the CaTiO$_3$:Al^{3+} system, a single peak appears for 1.5% Al, as shown in Fig. 7, which plots tan δ as a function of temperature for a selected frequency. In this case, the peak increases for the 5% sample, but then virtually disappears for the high (15%) concentration.

Table II summarizes the data for the principal peaks in all three systems. In it we use the notation that E_r is the activation energy and ω_{r0} is the preexponential for the relaxation frequency ω_r. Table II shows that the values of E_r are surprisingly low, compared to activation energies for hopping processes in these systems, (which range from 0.6 to 0.8 eV). However, the values of ω_{r0} are $\sim 10^{13}$ sec^{-1}, as one would expect.

The important question that now arises is: what is the origin of these discrete relaxation peaks? From detailed previous studies of M^{3+}-doped ceria, all of the obvious hopping reorientation processes due to the various paired defects are accounted for by relaxations taking place at higher temperatures and with higher activation energies (~ 0.5–0.6 eV),[21] leaving no obvious explanation for these low-activation-energy peaks. In other systems where low-activation-energy processes were observed, the concept of off-center ions was invoked, in which an ion can oscillate between two positions
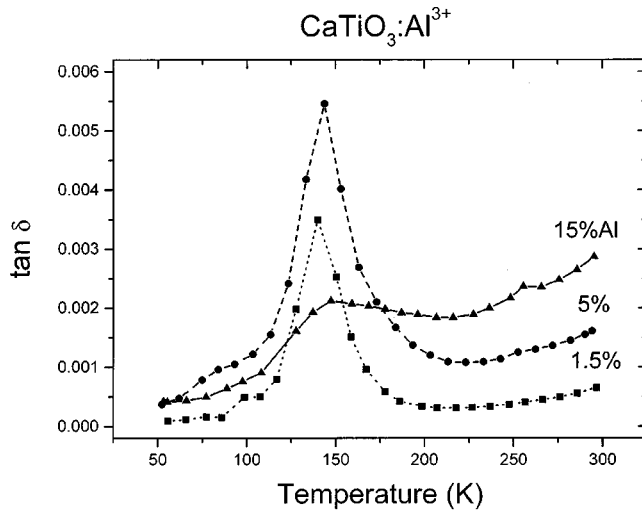
FIG. 7. Plots of tan δ, measured at 10^3 Hz, as a function of temperature for $CaTiO_3$ containing 1.5%, 5%, and 15% Al, showing the loss peak.

TABLE II. Summary of information on the principal discrete peaks. The quantity tan δ_{max} is the peak height.

Material	E_r (eV)	ω_{r0} (s^{-1})	10^3 tan δ_{max}
CeO_2:Gd^{3+}			
1%	0.28	3×10^{13}	1.5
2%	0.28	2×10^{13}	0.7
CeO_2:Y^{3+}			
1%	0.18	5×10^{12}	3.0
2%			0.5
$CaTiO_3$:Al^{3*}			
1.5%	0.27	2.5×10^{13}	3.5
5%	0.26	1.3×10^{13}	5.3

with a low activation energy.[38,39] However, following the discovery of a low-temperature relaxation process in Sc^{3+}-doped ceria,[40] a computer simulation study[41] showed that the relaxation in this case could be attributed, not to one ion moving off position, but to a cage of ions that surround the dopant going off symmetry in a very complex manner to produce a very low symmetry defect. According to these ideas, relaxation involves coordinated movements by less than an atomic spacing, which can better be described as ''rocking motions,'' in contrast to the ''hopping motions'' where an ion changes its site. (Jain[42] uses the picturesque term of ''jellyfish movements'' to describe such behavior.)

An interesting result is that, for both of the ceria systems studied here, the sample with 2% dopant already shows a decrease in peak height. This suggests that relatively large off-center configurations are involved, so that these configurations are perturbed by interaction with adjacent defects, even when the total defect concentration is as low as 2%. Even in the case of $CaTiO_3$:Al^{3+}, where the peak is higher for the 5% sample than for that of 1.5%, the ratio of peak heights is 1.5 (see Fig. 7 and Table II), well below the concentration ratio of 3.3. Finally the disappearance of the peak at high concentrations in each case goes hand in hand with the appearance of conventional NCL behavior in the concentrated samples. This result suggests that, in complex materi-

als, the discrete peaks have smeared out into a broad distribution of relaxation processes involving off-center configurations and rocking-type motions, as is particularly well illustrated by Fig. 7, where only a remnant of the peak remains for the 15% sample. We therefore believe that smearing out of discrete relaxations provides the basis for NCL behavior in complex materials. A surprising result, worthy of further investigation, is that such off-center configurations are so prevalent in these materials.

IV. CONCLUSIONS

In the UDR regime, simple materials show the same behavior as complex materials, leading to the conclusion that this type of electrical relaxation is intrinsic to the ion hopping process.

On the other hand, conventional NCL behavior is characteristic only of complex materials. Simple materials often show discrete relaxations that may be attributed to off-center defect configurations that relax by rocking-type motions. As the concentration of defects increases, these relaxations are smeared out into a broad distribution that gives rise to NCL behavior.

The present results also provide additional evidence that the UDR and NCL phenomena involve distinct and separate physical mechanisms.

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