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Dielectric response of Naβ-alumina: Evidence for a "glass transition"

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Electrical modulus (M'') data for melt-grown Naβ-alumina between 92 and 151 K is fitted in terms of the fractional-exponential-decay formalism with a fractional exponent n. Above 120 K the exponent n decreases rapidly with increasing temperature, whereas the M'' peak frequency shifts with temperature as predicted by the Williams-Landel-Ferry relation. The behavior of n and M'' is similar to that observed for glasses near their glass transition, which suggests that Naβ-alumina undergoes a "glass transition" near 120 K. It is also shown that the recent low-frequency-response model of Ngai yields the observed $n(T), M''(\omega, T)$ behavior and leads to the determination of the microscopic activation energy for Na$^+$-ion motion of 0.059 eV.

I. INTRODUCTION

The crystalline fast-ion conductor Naβ-alumina exhibits a large, liquidlike ionic conductivity at elevated temperatures (>300 K),[1] but glasslike dielectric,[2,3] thermal,[4] and acoustic[5] properties at low temperatures (<50 K). This unusual behavior is due to the inherent configurational disorder among the mobile Na cations within the rigid crystalline host lattice. It is of fundamental interest to understand how the transition from a glasslike to a liquidlike phase takes place. In this paper, the available data in the transition region from 50 to 300 K are briefly reviewed. It will be shown that recent dielectric loss data of Almond and West,[6] when interpreted in terms of a fractional-exponential response theory,[7] shows a behavior which is characteristic of glasses and polymers near their glass transitions. The glass transition[8,9] is generally considered to be a phenomenon associated with very slow molecular rearrangement processes, and high viscosity typically of the order of 10^{13} poise. Above the glass-transition temperature T_g, the structure rearranges readily in response to changes or perturbations and full thermodynamic equilibrium is achieved. Below T_g, the structural rearrangement is kinetically arrested and the system falls out of complete thermodynamic equilibrium. The glass transition is accompanied by changes in physical properties such as specific heat, expansion coefficient, etc. Often, but not always, the viscosity near T_g departs from Arrhenius behavior with a temperature-independent activation energy. This behavior is well described by the Vogel-Tamman-Fulcher empirical equation.[10] Also near T_g, the "shift factor" of dielectric and mechanical relaxations obeys the Williams-Landel-Ferry (WLF) empirical equation[11] rather well.

The large dc ionic conductivity (0.02 Ω^{-1} cm^{-1} at 300 K) of Naβ-alumina has been interpreted as due to the cooperative motion of pairs or larger groups of Na ions.[12] The Na ions occupy well-defined sites in the conduction planes of the β-alumina structure. Because of an excess of Na above the stoichiometric value[13] and the presence of additional charge compensating oxygen ions in the conduction planes,[14] the arrangement of neighboring ions near a given Na ion may spatially vary. A variety of ion configurations may exist which are changing rapidly in size and shape at elevated temperatures. Specific cases of configurations have been proposed by Wolf.[15] In a qualitative sense, the mobile ions resemble a (two dimensional) "liquid." At lower temperatures, the ion configurations become increasingly less mobile. Diffusive x-ray measurements[16,17] show only a small increase in conduction plane long-range order at lower temperatures, which indicates that there is *no* transition to a crystalline cation sublattice in Naβ-alumina. In fact, low temperature dielectric and thermal measurements below 50 K in Naβ-alumina exhibit the behavior typical of glasses.[2-5]

The transition region from 50 to 300 K has been studied in terms of specific heat[18] and nuclear magnetic resonance (NMR).[19,20] A very broad maximum is observed in the specific heat near $T\sim 120$ K. This peak is similar to the specific-heat peak which is generally observed in glasses and polymers near their glass transitions and has been interpreted by Bjorkstam *et al.*[18] as evidence for a "melting" process. The significance of this peak becomes clearer in view of the results of the ^{23}Na NMR as a function of temperature. NMR is a sensitive probe of the local environment around a ^{23}Na nucleus. This environment may be different in the high-temperature and low-temperature phases. Bjorkstam, Villa, and Farrington[20] have observed two ^{23}Na NMR lines in Naβ-alumina which coexist at temperatures less than 90 K, but only one of which is observed for $T > 170$ K. The most rapid change in NMR amplitudes of the two observed lines occurs near $T \sim 120$ K. They interpret this behavior as due to the formation of "ordered microdomains" in the conduction planes as the temperature is lowered below ~ 120 K, an interpretation which is consistent with the specific-heat results.

Recently, Almond and West[6] have published dielectric loss data of Naβ-Al$_2$O$_3$ which they present in the complex electric modulus (M^*) formalism[21] in which M^* is the inverse of the complex permitivity. This formalism is appropriate for ionic conductors which are sufficiently highly conducting such that the conductivity dominates the dielectric loss. Moreover, $M^*(\omega)$ directly reflects the distribution of hopping relaxation times and is more informative. Jonscher[22] has proposed for *dipolar* relaxations (i.e., not mobile charges) an empirical formula for the dielectric loss $\chi''(\omega)$:

$$1/\chi''(\omega) \propto (\omega/\omega_1)^{-m} + (\omega/\omega_2)^{1-n} ,$$

where ω_1 and ω_2 are thermally activated parameters and m and $1-n$ are exponents. Almond and West assert that this empirical formula for relaxation of permanent dipoles is also valid for the imaginary part of the electric modulus $M''(\omega)$, which is appropriate for mobile charged carriers. Almond and West[6] have also made mention of a weak temperature dependence of their model parameters m and n but did not attach any special significance to this observation. We present here an alternate analysis of their data in terms of the empirical fractional-exponential-decay formalism.[21] Our results can be summarized as follows: (1) The fractional-exponential-decay model provides a good fit to the data; (2) the fractional exponent is observed to be temperature dependent in the same temperature range where specific-heat and NMR anomalies occur; (3) the temperature variation of the exponent is comparable to that observed for glasses near their glass transition.

II. EXPERIMENTAL RESULTS

A. Fractional-exponential decay

In ionic conductors the local hopping motion of ions over potential barriers can lead to long-range ionic transport. The associated contribution to the dispersion in the complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ will compete with a contribution due to local ion motion which does not lead to ionic transport. Macedo, Moynihan, and co-workers[21] have shown that for the purpose of analyzing dielectric relaxation due to mobile carriers in dielectrics, it is appropriate to consider the inverse complex permittivity $M^* \equiv 1/\epsilon^*$, where M^* is called the electric modulus. M^* characterizes the dynamic aspects of ion motion in vitreous ionic conductors in terms of the relaxation of the electric field. The decay of the electric charges on opposite faces of the sample are described by $E(t) = E(0)\phi(t)$. The decay function $\phi(t)$ is generally nonexponential. In the frequency domain the electric field relaxation is described by

$$M^*(\omega) = M_\infty \left[1 - \int_0^\infty dt \exp(-i\omega t) \frac{-d\phi(t)}{dt} \right] \tag{1}$$

where M_∞ is the high-frequency limit of the real part of M^* and ω is the angular frequency. The dc conductivity σ_0 is related to the average electric field relaxation time $\langle \tau_0 \rangle$, given by

$$\langle \tau_0 \rangle = \int_0^\infty dt\, \phi(t) \equiv \lim_{\omega \to 0} \left[\frac{\mathrm{Im} M^*(\omega)}{\omega} \right] , \tag{2}$$

by

$$\sigma_0 = \epsilon_0 / M_\infty \langle \tau_0 \rangle , \tag{3}$$

where ϵ_0 is the permittivity of free space.

Macedo *et al.* have applied the electric modulus method to vitreous ionic conductors, including alkali silicate glasses and the glass-forming salt Ca(No$_3$)$_2$-KNO$_3$. They found the observed frequency dispersion in M^* can be empirically described in terms of the nonexponential decay of the electric field of the form

$$\phi(t) = \exp[-(t/\tau_p)^\beta] , \quad 0 < \beta \le 1 \tag{4}$$

where τ_p is a characteristic relaxation time. When $\beta = 1$, the decay is exponential with a single conductivity relaxation time. The M^* data for various alkali silicate glasses and for the glass-forming salt were analyzed successfully in terms of Eq. (4).[21] Of course, for an equivalent description of data by ϵ^*, M^*, or σ^* the experiment must be performed in the small signal or linear regime.

In a similar manner the M^* data for Naβ-alumina at a single temperature $T = 113$ K has been recently analyzed and shown to be well fitted by the fractional exponential with $\beta = 0.35$.[23] The data and fit correspond to the $T = 113$ K curve in Fig. 1 with $\beta \equiv 1 - n$. There are two parameters involved in this fit, namely n and τ_p. The dispersion or shape of the

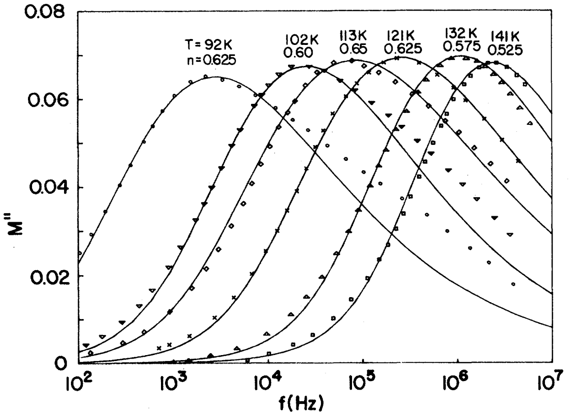

FIG. 1. Electric modulus data (Ref. 6) for various temperatures. Solid curves, theoretical fits (present work).

$M''(\omega)$ peak depends only on n, while τ_p determines the position of the peak. Considering that the ionic conductors cited above have very different physical and chemical structures, it is remarkable that the class of fractional-exponential-decay functions describe so well the relaxation due to ion hopping motion. Previously[7] it has been shown that for permanent dipole relaxations, the observed dispersion in ϵ^* is also well described by the fractional-exponential-decay function [Eq. (4)], which suggests its very general applicability to diverse dielectric phenomena.

B. Temperature dependence of electric modulus

In the preceding section it was shown that dispersion of the electric modulus data for various ionic glasses and Naβ-alumina were well described empirically at a given temperature by the fractional-exponential time-decay formalism. Equally good fits in the case of glasses have been obtained at other temperatures which span the glass-transition temperature T_g. Such fits require that the parameters τ_p and β are temperature dependent. Specifically, β *exhibits a nearly steplike change near* T_g. Two examples, which illustrate this behavior, are shown in Figs. 2 and 3. In Fig. 2 the substance bromobenzene (11.1 mole%) in supercooled decalin is known to undergo a glass transition near $T_g \sim -137\,^\circ\mathrm{C}$ (136 K).[24] The insets to Fig. 2 show the data of the normalized imaginary part of dielectric susceptibility $\chi''/\chi''_{\max}$ plotted versus normalized frequency $f/f_{\max}$ at five different temperatures, where $f_{\max}$ denotes the frequency when $\chi''=\chi''_{\max}$. The dielectric loss peak at each temperature is well fitted by the Fourier transform of the derivative of the fractional exponential function (solid curves in each inset). The fractional exponent $n \equiv 1-\beta$, where β is defined in Eq. (4), is found to be temperature dependent. As seen in Fig. 2 the parameter n is seen to *decrease* from $n \cong 0.78$ near T_g to $n=0.63$ at a temperature ~ 5 K above T_g. The second example is the polymer PVAC (polyvinylacetate) shown in Fig. 3.[25] The insets represent the data ($\chi''/\chi''_{\max}$) and appropriate fits as a function of $f/f_{\max}$ for different temperatures. In this case the fitting parameter n has a cusplike maximum near $T_g \sim 20.5\,^\circ\mathrm{C}$. Again n decreases from 0.57 to 0.475 as the temperature is raised $\sim 30\,^\circ\mathrm{C}$ above T_g.

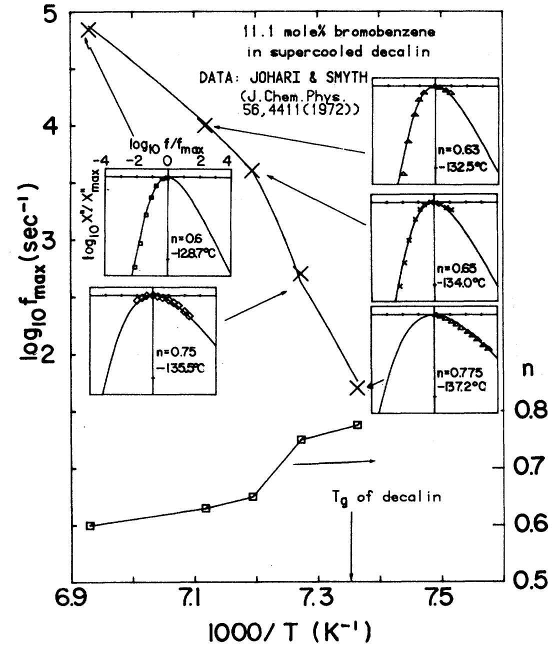

FIG. 2. Dielectric susceptibility of 11 mole% of bromobenzene in supercooled decalin at different temperatures near glass transition ($\sim -137\,^\circ\mathrm{C}$). Solid lines in insets: theoretical fits with fractional exponent n.

The appropriate fits for Naβ-alumina using the single—fractional-exponential formalism were shown in Fig. 1. The fit deteriorates at the lowest two temperatures but at the high-frequency side only. The excess contributions in this regime are most likely due to excitation of tunneling modes via the relaxation mechanism.[3] Contributions to the ac conductivity due to such modes cannot be described in terms of the hopping formalism of Eqs. (1)—(4) and thus must be considered as physically distinct contributions to the dielectric loss or electric modulus. The variation of β and $f_{\max} \equiv 1/2\pi\tau_p$ with temperature are shown in Fig. 4. A marked

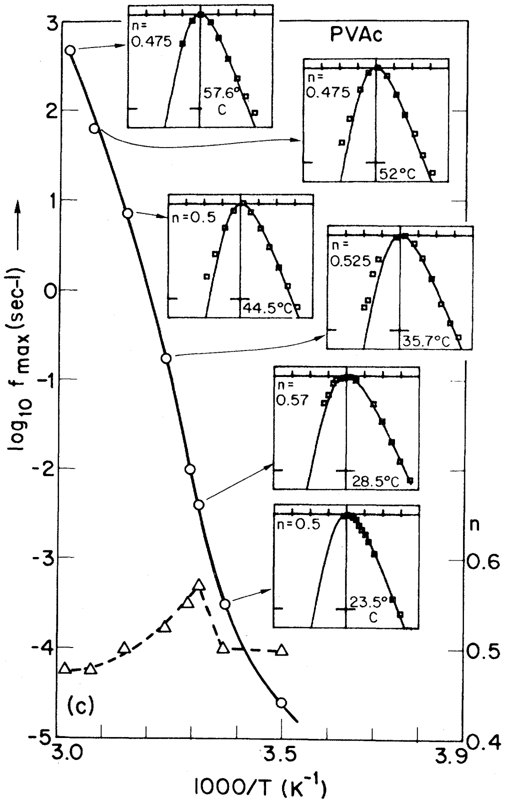

FIG. 3. Dielectric susceptibility of polyvinylacetate (PVAc) near glass transition, (~28.5 °C). Solid lines in insets: theoretical fits with fractional exponent n.

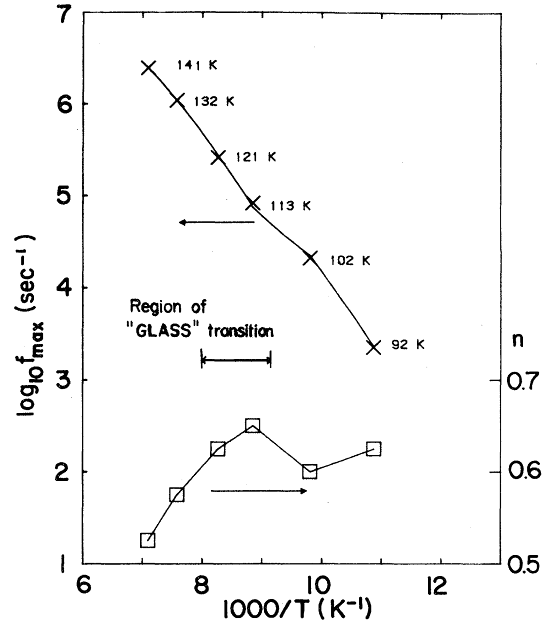

FIG. 4. Variation of $\beta \equiv 1-n$ and $f_{\max}$ with temperature. Upper curve, $f_{\max}$ (crosses, experiment; solid lines, theory). Lower curve, $n(T)$ from fits as shown in Fig. 1.

change in the slope of $n(T)$ vs $1/T$ is observed near $T \sim 120$ K. In addition, the plot of $\log f_{\max}$ vs $1/T$ exhibits a noticeable departure from Arrhenius behavior (i.e., straight line on a $\log f_{\max}$ vs $1/T$ plot). In particular, for $T \geq 113$ K the experimental points fall on a curve that is convex upwards. This temperature variation of $f_{\max}$ resembles the WLF behavior[11] for dielectric and viscoelastic relaxation of glasses and polymers above and near T_g as shown by the examples in Figs. 2 and 3.

III. DISCUSSION

The results presented above suggest that Naβ-alumina undergoes a glasslike transition near $T \sim 120$ K. This conclusion is supported by recent NMR measurements of Bjorkstam, Villa, and Farrington[20] who observed that the ^{23}Na NMR line observed at $T = 300$ K and below decreases rapidly in magnitude for $T < 150$ K. At the same time a second line at slightly lower frequency appears which Bjorkstam *et al.* interpret in terms of ^{23}Na located in "ordered microdomains." In Fig. 5 the NMR and electric modulus data are directly compared. We have plotted the fractional exponent n and the normalized NMR intensity of the higher frequency ^{23}Na peak. The onset of the change in n with T, which generally marks the glass transition, is shown to correspond closely to the maximum rate of change of the ^{23}Na NMR intensity. Thus the temperature dependence of NMR in Naβ-alumina provides evidence for a structural change near $T \sim 120$ K, which is consistent with the conclusions drawn from our analysis of the electric modulus data. Also shown in Fig. 5 is specific-heat data for Naβ-alumina over the same temperature range. The peak in the specific heat near 125 K has been interpreted generally as evidence for melting of the cation sublattice, which supports the hypothesis that upon cooling below ~125 K Naβ-alumina approaches a glasslike phase. It should be stressed that there is little doubt about the existence of the low-temperature glasslike phase. The point made here is that the dielectric measurements exhibit a distinct behavior which points to the existence of a "glass transition" near $T \sim 120$ K.

Our arguments up to now have been based on fits to the dielectric data with the empirical fractional-exponential-decay formalism, as was previously proposed by Macedo, Moynihan, and co-workers.[21] In

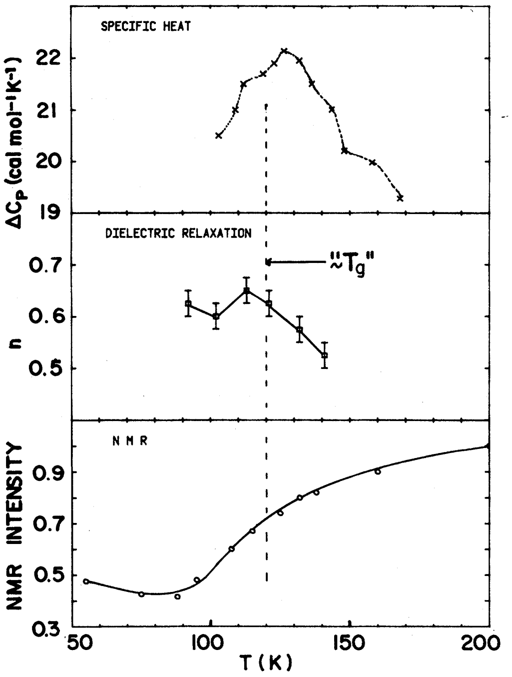

FIG. 5. Comparison of specific heat, ^{23}Na NMR relative peak intensities, and fractional-exponential exponent (n) for Naβ-alumina as function of temperature.

the subsequent discussion we will briefly examine an alternate approach, the infrared divergence response model (IDR),[7] which yields identical fits to the electrical modulus data as was obtained with the empirical fractional-exponential fit, but in addition predicts a microscopic activation energy for ionic motion which can be directly compared with the activation energy obtained from low-temperature NMR measurements. This model can address the question of the position $f_{\max}$ of the $M''(\omega)$ peak and its temperature dependence. According to the IDR model, the ion relaxation rate τ_0^{-1} will be modified to the time-dependent function[7]

$$W(t)=\tau_0^{-1}e^{-n\gamma}(\omega_c t)^{-n} , \tag{5}$$

where $\gamma=0.577$ is the Euler constant, ω_c and $0\leq n<1$ are IDR parameters. The rate equation for hopping relaxation of the Na$^+$ ions described by $dQ/dt=Q/\tau_0$, with Q being the probability that an ion initially residing at a site will remain there at time t, is then modified to

$$\frac{dQ}{dt}=-\tau_0^{-1}e^{-n\gamma}(\omega_c t)^{-n}Q , \tag{6}$$

which has the solution

$$Q=Q_0\exp[-\tau_0^{-1}e^{-n\gamma}t^{1-n}/(1-n)\omega_c^n] . \tag{7}$$

For the special case $n=0$, Eq. (8) reduces back to $Q=Q_0\exp(-t/\tau)$. For $n\neq0$ Eq. (8) yields the fractional-exponential form $Q=Q_0\exp(-t/\tau_p)^{n-1}$. This is identical to the form in Eq. (4) where we identify $\beta=1-n$ and

$$\tau_p^{-1}=[e^{-n\gamma}/(1-n)\tau_0\omega_c^n]^{1/(1-n)} . \tag{8}$$

If τ_0 is thermally activated such that $\tau_0(T)=\tau_\infty\exp(E_A/kt)$, where E_A is the *microscopic* activation energy, then Eq. (8) can be rewritten as

$$\tau_p=\tau_\infty^*\exp(E_A^*/kT) , \tag{9}$$

where

$$\tau_\infty^*=\tau_\infty[e^{n\gamma}(1-n)(\omega_c\tau_\infty)^n]^{1/1-n} \tag{10}$$

and now $f_{\max}$ will shift with temperature as $\exp(E_A^*/kT)$ with an apparent activation energy

$$E_A^*=E_A/(1-n) \tag{11}$$

provided n and ω_c are temperature independent.

The peak position of $M''(f)$ vs f as in Fig. 1 is found at $f_{\max}$ such at $2\pi f_{\max}=\tau_p^{-1}$. The empirical formalism [Eq. (4)] assumes τ_p to be a fitting parameter, whereas τ_p given in Eq. (9) exhibits a predictable dependence on the fractional exponent n. Thus we expect a close relationship between the temperature dependence of n and $f_{\max}$. The fitting procedure of the data in Fig. 1 proceeds as follows. Each curve of M'' vs f is least-square fitted to determine the optimum value of the fractional exponent n at each temperature. With $n(T)$ known for six temperatures, a least-square fit is made to the experimentally determined frequencies $f_{\max}(T)$ by varying the three parameters E_A,ω_c, and τ_∞. The fit is shown by the solid lines drawn between the $f_{\max}(T)$ data points (crosses) in Fig. 4. To a first approximation, this fit assumes no temperature dependence for ω_c and τ_∞. As seen in Fig. 4, good agreement with experimental data for $f_{\max}(T)$ is attained, which also justifies the neglect of the temperature dependence of ω_c and τ_∞. In the process, E_A,ω_c, and τ_∞ are determined. We find that $E_A=0.059$ eV, $\omega_c=1.2\times10^8$ sec^{-1}, and $\tau_\infty=2.7\times10^{-10}$ sec. The magnitude of ω_c can be related qualitatively to a frequency above which the ac conductivity in Naβ-alumina approaches a frequency-independent regime[26] which reaches up to the onset of the strong lattice absorption above $\sim10^{11}$ sec^{-1}. The value for E_A determined here from the low temperature 141 to 92 K data is in remarkable agreement with the value of 0.058 eV determined earlier from internal friction and NMR spin-lattice relaxation.[19,27] Furthermore, Eqs. (10) and (11) predict the existence of an effective activation energy $E_A^* = E_A/(1-n)$ and effective relaxation time τ_∞^*. As discussed previously,[23] E_A^* can be associated with long-range diffusive transport. With the range of n determined to fall between ~ 0.52 and 0.65 we predict values of E_A^* between 0.12 and 0.17 eV. These values span the measured dc activation energy of 0.16 eV which has been observed between 120 and 1000 K. It is uncertain whether the transport data reaches sufficiently low temperatures to discern the temperature-dependent activation energy which is predicted by the above formalism.

IV. SUMMARY

We have shown that electric modulus M'' data for Naβ-alumina near $T \sim 120$ K give valuable insight into the structural changes taking place near 120 K. The M'' data are remarkably well fitted by the fractional-exponential-decay function for all temperatures. For $T > 120$ K the fractional exponent is a function of temperature. The M'' peak frequency shifts with temperature according to the WLF empirical relation for $T > 120$ K, very much like the behavior in glasses and polymers near and above the glass-transition temperature. These similarities furnish strong evidence that the structural changes observed by NMR near $T \sim 120$ K in Naβ-alumina can be interpreted as a "glass transition" in the cation sublattice.

It was also shown that a recently proposed model of low-frequency response in solids applied to Naβ-alumina yields the observed fractional-exponential decay and the WLF behavior of the M'' peak frequency. The quantitative fit of the model to the electric modulus data led to the determination of the microscopic activation energy E_A of 0.059 eV, in agreement with separate earlier determinations of E_A.

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