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Thermally stimulated polarization-depolarization current and polarization conductivity in ionically conducting glasses

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The polarization conductivity $\sigma'(\omega)$ of Na_2O-$3SiO_2$ glass has been studied by impedance spectroscopy (100 Hz–5 MHz). The results are explained on the basis of a free-volume model applied to ionically conducting glasses. The experimental relationship $\sigma'(\omega)=A\omega^S$ was found and the parameter s calculated according to the model. The distribution of relaxation times included in the expression of $\sigma'(\omega)$ was evaluated by thermally stimulated polarization-depolarization current peaks attributed to the bulk polarization. The experimental results related to $\sigma'(\omega)$ and parameter s were compared with the calculations performed by means of a distribution function, determined by the thermally stimulated current technique. There is good agreement between the results showing that the two approaches are complementary.

I. INTRODUCTION

The interpretation of transport properties in ionically conducting glasses actually uses different approaches. However in most interpretations, the fundamental hypotheses use the same elementary mechanism to describe the polarization conductivity,[1–18] i.e., hopping ions which cross a potential barrier separating two sites.[19] The differences appear in the developments which lead to a mathematical expression accounting for the evolution of the hopping process as a function of time. In this context the notion of mobility of charge carriers is a concept which refers generally to statistical distributions[20] to account for possible disparities of behavior within the population of the charge carriers considered. Our purpose is to make this notion of mobility a conceptual tool sufficiently broad to interpret the characteristic properties of materials where the phenomena related to current transport can be ascribed to ionic motion. In this view the thermally stimulated depolarization currents (TSDC) method which will be presented, can prove particularly useful.

II. POLARIZATION CONDUCTIVITY

A. Modelization of the polarization conductivity in ionically conducting glasses

If we are interested by solids which are poor electric conductors, it can be shown that the electric field can penetrate into such materials and act on the charge carriers present in the sample, from which comes the name "dielectric" given to this family of compounds. But the charge carriers found in these materials are no longer free since they cannot move easily under the action of the field as in the case of diffusion. They are called "bound charges."[18] From a macroscopic point of view, the descriptions of the electric state of a dielectric by a polarization distribution or by a bound-charge distribution are equivalent.

In the case of ionic glasses, the sample can be considered as a noncompact assembly of atoms moving under the action of thermal agitation. It is unlikely that an atom set into such a medium can move if all its neighboring atoms do not move as well.[21,22] On the contrary, the motion of the ion considered is only due to the cooperation of the motion of each neighboring atom. This ion then cannot move unless a thermal agitation exists.[23,24] This system must then be held above a critical temperature.[12,13]

When an alternating current is applied, a polarization conductivity appears due to discrete hops of charge carriers. In the absence of a field these charge carriers are localized within sites, in a given volume, called "free volume," where their motion is reduced to weak oscillations due to thermal agitation. The fluctuations in the solids, around the equilibrium state, give rise to a redistribution of the free volume associated with the particles and the association of the free volumes allows the hopping of ions over short ranges.[25,26] The system of hops can be represented as analogous to a dipole reorientation. As long as there is no electric field applied, each dipole is randomly distributed and the resulting dipolar moment is

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zero. When an alternating field is applied, these dipoles are partially aligned according to the direction of the field. A macroscopic dipolar moment appears and attempts to follow the evolution of the field, i.e., its rapidly changing direction: a polarization conductivity appears.

The polarization conductivity is then ascribed to the local motion of ions, moving around their equilibrium position over a short period of time. They do not participate in a diffusional macroscopic motion.

Accounting for this elementary microscopic process, we used a model of free-volume fluctuations, associated with particles.[18] In this way, we expressed the potential barrier between localized sites as a sum of two terms, one related to a configuration state, the other to electrostatic forces.[9] This barrier is then introduced in the calculations of the polarization conductivity, making use of the models already developed.[6–9,18] We point out the analogies in the behavior of the different carriers moving in a solid:

(1) The law explaining the experimental results keeps the same mathematical form, whatever the charge carriers, and has consequently been called universal[17]

$$\sigma'(\omega)=A(T)\omega^{s(T,\omega)} . \tag{1}$$

(2) The expression of the relaxation time associated with the hop over a potential barrier W, keeps the same mathematical form:

$$\tau=\tau_0\exp\frac{W}{kT} .$$

We proceed then to a description of microscopic process taking into account the interactions between the charge carriers and the neighboring atoms. This means that the potential barrier that an ion must cross is not only a function of the hopping distance. We attempted to account for this cooperative phenomenon by explaining the energies involved in the elementary mechanisms of charge transport. The motion of these ions is ascribed to the creation of free spaces, the dimension of which exceeds a critical value.[21,22,26] The fluctuations induced by the thermal agitation create spaces sufficiently large to induce charge transport within short-range distances.

This mechanism is well adapted to describe the polarization conductivity with bound charges, since it does not involve long distance hops. Indeed, this does not mean that these charge carriers do not participate in the diffusion conductivity nor that the hopping process cannot be partly included in a description of the diffusion conductivity. We only emphasize that the mechanism described here gives a satisfying picture of an elementary hop implied in the polarization conductivity. Considering the frequency domain used in this work, we propose a representation of one of the movements of the charge carriers, connected to the bound-charge notion.

We note that this description of the microscopic process responsible for the polarization conductivity is consistent with the thermodynamic interpretation proposed to account for the displacement of charged species in these same kinds of materials.

In fact, the fluctuations do not interfere in the distribution laws used in the theory of weak electrolytes, for instance.[27] In order to continue the calculations, we have to establish a relation between the hopping distance R and the height of the potential barrier W. According to this description it seems natural to consider that this barrier arises from the sum of two terms[9,18,19]

$$W=W_e+W_g ,$$

where W is the potential barrier, W_e the electrostatic energy, and W_g the configuration energy of the structure. The term W_g is connected with the geometry of the system and is described using the concept of fluctuation. These fluctuations around the thermodynamic equilibrium state of the system, are essentially related to the temperature.[18,28,29]

In first approximation we can express this energy as: $W_g=\eta kT$, where η is in empirical parameter. Its physical significance has been defined in a previous study, proposing a microscopic description based on fluctuations applied to a system of interacting particles representing the ionically conducting glass.[18]

B. Expression of the conductivity $\omega'(\omega)$

The conductivity, determined as a function of frequency, takes the form, $\sigma_{\text{ac}}=\sigma_0+\sigma'(\omega)$ whatever the nature of the solid. In this expression σ_0 is independent of the frequency throughout the domain studied. Henceforth we cannot account for the behavior of the polarization conductivity in ionically conducting glasses by expressing hypotheses leading to[11–13]

$$\sigma'(\omega)=\int_0^\infty G(\tau)\frac{\omega^2\tau}{1+\omega^2\tau^2}d\tau . \tag{2}$$

We have shown that in this interpretation it is essential to know the distribution function $G(\tau)d\tau$ characterizing the population of dipoles.[30,31] Making a series of hypotheses on ion motion in these glasses, we were able to propose an estimate of this distribution and we have determined a law describing the evolution of the polarization conductivity as a function of frequency.[31] We showed that the same mathematical form is obtained whatever the nature of the charges involved, provided their behavior is characteristic of bound charges: $\sigma'(\omega)=A(T)\omega^{s(T,\omega)}$.

We see that the law describing the variation of the polarization conductivity as a function of frequency can be discussed mathematically in the same way, whatever the solid under study. In these circumstances the variation of the exponent s, as a function of temperature, can give information on the nature of the charge carriers. In fact, in the proposed representation, the charge carrier motion is due to the cooperative displacement of each neighboring atom. In these models the interaction between the hops and the thermal movement of neighboring atoms is considered. We showed[18] that the exponent s could be written[30–32]

$$s=1-\frac{\gamma kT}{W_e+kT\ln(\omega\tau_0)+\eta kT} . \tag{3}$$

C. Physical meaning of the exponent s

Henceforth, the representation of the population conductivity can be extended to all compounds where the notion of discrete hops can be implemented, in an attempt at modelization. The polarization phenomenon induced by an alternating electric field creates a current ascribed to the bound-charge motion similar to hops between localized sites.

It is obviously impossible to differentiate a free-charge carrier from a bound-charge carrier since, by definition, they are indistinguishable. It is only a matter of a suitable classification referring to two specific states of charge carriers. The exponent s then appears as connected to the ratio of the thermal movement of the charge carriers to the energies that trapped them in their sites. In the expression of s, this ratio is weighted by a parameter γ, which appears to be proportional to the degree of freedom of the movement of the considered ions.

III. EXPERIMENTAL RESULTS

After these theoretical considerations, we have undertaken an experimental study with the aim of validating or refuting the fundamental hypotheses expressed to describe the model of the polarization of conducting glasses.

It was firstly a matter of measuring the polarization conductivity of a well-known glass so that the uncertainty on the experimental values and on the derived relationships were as low as possible. We chose to observe the behavior for glassy Na_2O-$3SiO_2$ the properties of which have been carefully investigated.[33–36] We had then to determine the characteristic dipole population equivalent to the "bound charge" distribution. In this view we observed the behavior of the thermally stimulated currents TSDC in the samples on which the polarization conductivity had been already measured. Finally we compared the experimentally determined parameters in both cases, following a procedure developed in order to confirm the validity of the theoretical approach.

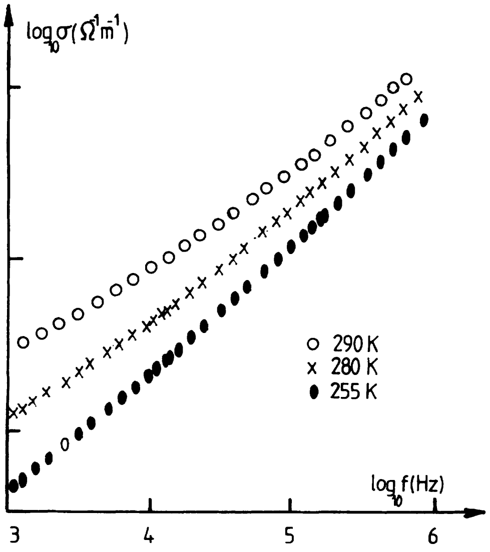

FIG. 1. Polarization conductivity as a function of frequency of Na_2O-$3SiO_2$ glass at 255, 283, and 300 K.

A. Measurements of the polarization conductivity

We measured the polarization conductivity of samples between 100 Hz and 5 MHz. The use of high impedance electrodes described in detail in a previous work,[36] enabled the polarization conductivity within a temperature range of 240–310 K to be determined.

The polarization conductivity as a function of frequency is represented in Fig. 1 (in a log-log scale) for three different temperatures taken as examples. We note that over all the considered frequency range, the law, $\sigma'(\omega)=A\omega^{s(T,\omega)}$, is respected. In Fig. 2, the evolution of the exponent s, calculated at 4.5 kHz as a function of the measured temperature has been plotted.

B. Experimental determination of fundamental parameters of the polarization by thermally stimulated current measurements

The experimental results have obtained on samples, the polarization conductivity of which had been investigated by observing the behavior, as function of temperature, of the thermally stimulated current. The measurements have been performed by means of a thermally stimulated current/relaxation map analysis (TSC/RMA) spectrometer, model 9100+, of Solomat Instrumentation.

The TSC method consists of determining, following a strictly controlled temperature program, either the current created by the return to an equilibrium state of a dielectric which has been previously polarized (TSDC), or the charge current resulting from a thermally activated transition, obtained by passing from an equilibrium state to a polarized state [thermally stimulated polarization current (TSPC)].[37]

This kind of experience generally takes place in four steps:

(1) a direct voltage V_p is applied to the sample at temperature T_p ($V_p=0$ in the case of TSPC).

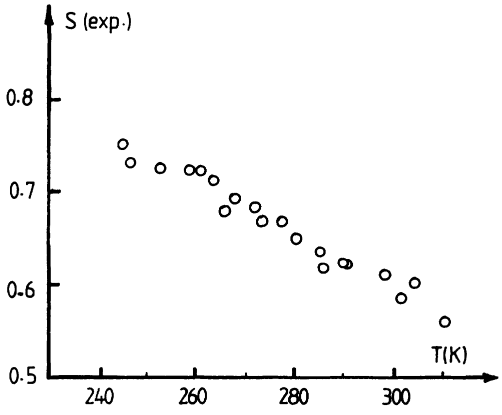

FIG. 2. Temperature dependence of parameter s, at $f=10^{4.5}$ Hz.

(2) the sample is cooled and the voltage V_p remains applied, until a temperature T_f is reached.

(3) the polarization voltage is modified and takes a new value V_d ($V_d=0$ in the case of TSDC).

(4) the sample is warmed up following a rigorously controlled program of temperature, the law of evolution being usually linear. During this last step we can observe the current induced by the depolarization (TSDC) or the polarization (TSPC) of the sample.

In the cases considered, we attempt to display the polarization due to ion motion, with the help of a model referring to a dipole population.

When such a sample, previously polarized, is warmed up above a fixed temperature T_i, we can observe a current induced by the charge relaxation considering that some motion parameters can be considered as being characterized by this temperature. When the relaxation time τ_i of a category of dipoles in the sample becomes comparable to that of the measurement, determined by the heating rate, the associated phenomenon becomes measurable and induces a current in the external circuit, as predicted by the polarization theory.

In the case of ionically conducting glasses the observed polarization characterizes materials containing localized sites due to the presence of ions. It is due to the separation of the positive charge barycenter from that of the negative charge, under the action of the electric field. It creates a macroscopic phenomenon the relaxation time of which can vary over a very large time scale.

Scanning the temperature domain, we can observe a complex evolution of the polarization current (Fig. 3). As shown in Fig. 3, the DSDC and TSPC peaks are characterized by the same position, height, and shape. The only difference is that they appear in opposite directions. This is a clear indication of the dipolar nature of the processes involved.[37,38]

The TSDC peak can be deconvoluted by the "thermal-windowing" technique,[37,39–41] which consists of polarizing only a fragment of the full spectrum of relaxation and depolarizing it partially to isolate a "single" relaxation process. By varying the value of the temperature of polarization T_p and depolarization T_f ($T_p-T_f=5$ °C in our case), and repeating the process over the entire range, the elementary modes can be isolated one by one. This unique feature of the TSD method allows the elementary relaxation and activation energies W_i to be determined by assuming a classical temperature dependence of τ_i following

$$\tau_i(T)=\tau_0\exp\left[\frac{W_i}{kT}\right].$$

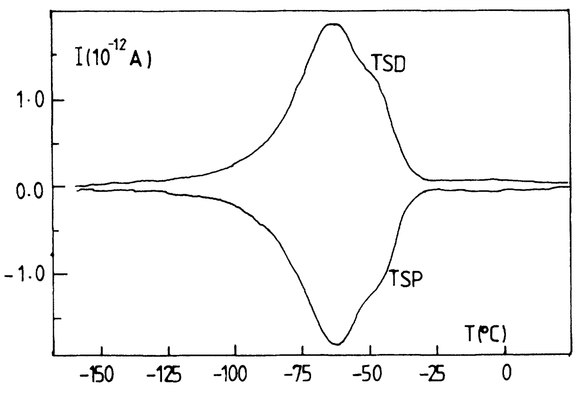

FIG. 3. Variation of polarization and depolarization current as a function of temperature for Na_2O-$3SiO_2$.

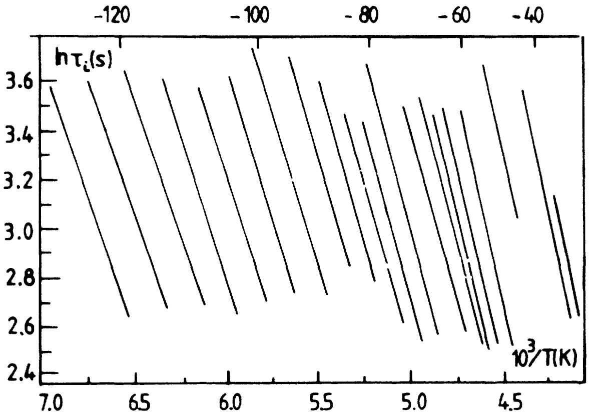

FIG. 4. Relaxation map obtained from TSDC elementary peaks deconvoluted by the thermal windowing technique in the −120 to −25 °C range.

The collection of relaxation lines deduced from each deconvoluted peak (relaxation map[41]) is represented in Fig. 4, and the values of the corresponding activation energies are reported in Fig. 5.

Thus the analysis of TDSC results gives the possibility of evaluating directly the polarization distribution as a function of temperature, as P_i is proportional to the peak ordinate on the graph $I=f(T)$ (Fig. 3).

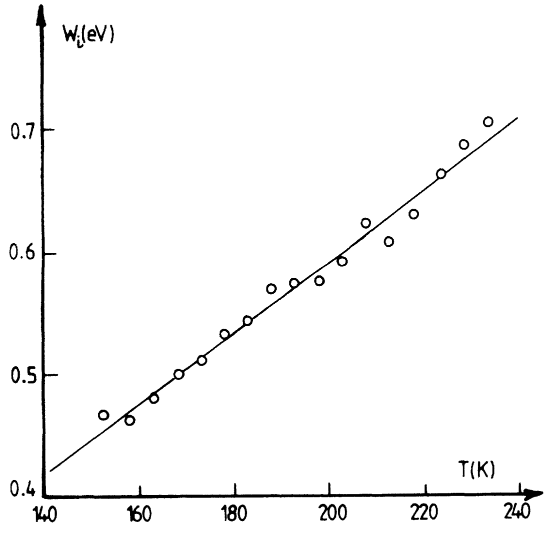

FIG. 5. Variation of the activation energies as a function of temperature (values obtained from the straight lines of Fig. 4).

IV. DISCUSSION

The polarization conductivity has been measured and we have accounted for its behavior. We have seen that it is essential to know the function $G(\tau)$ characterizing the population of dipoles.

Moreover, measurements of the thermally stimulated currents have permitted the determination of the potential barrier energies associated with each kind of hop, and the corresponding intensities representing the dipolar distribution. This series of measurements allows the reconstitution of the function $G(\tau)$. It is possible to determine to what extent the hypothesis that we have expressed is confirmed by experiment, when $\omega\varepsilon''(\omega)$ calculated from the measurements obtained by TDSC is compared to $\sigma'(\omega)$ obtained from complex impedance measurements.

A. Evolution of the energy connected to a hop

We found experimentally that the potential barrier W_i is a linear function of temperature (Fig. 5). This behavior is consistent with the hypothesis which supposes that it is possible to express the potential barrier in the form of two terms: one, due to the Coulomb forces, is temperature independent; the other, resulting from the free-volume fluctuations in the solid, varies obviously with the thermal agitation; we have already ascribed to it an expression of the form of ηkT.

If the linear behavior is analyzed by means of a least-squares method, the following equation is found:

$$W_i(eV)=0.0027T+1.165\times10^{-3} .$$

To investigate the physical signification of this energy can prove interesting. Indeed the relaxation time τ is the inverse of the hoping probability of an ion out of its site. In the glass studied the temperature for which this probability becomes a certainty is:[33] $\tau=1$, for $T=T_g$, and $T_g=756$ K. T_g is the glass transition temperature.

This value introduced in the expression of the relaxation time gives

$$\ln\tau=\ln\tau_0+\frac{W(T_g)}{kT_g} ,$$

leading to

$$\log_{10}\tau=\log_{10}\tau_0+13.6 .$$

This last result confirms the significance ascribed, in the view of our model, to the movement of the surrounding atoms in the hopping process. If $\tau=1$, as proposed for $T=T_g$, τ_0 takes an expected value, i.e., 10^{-13}–10^{-14} s.

B. Comparison of the results of both methods

If our hypotheses are consistent it should be possible to obtain the measurements of the polarization conductivity determined by impedance spectroscopy, from the parameters calculated when evaluating the polarization by the technique of thermally stimulated currents. Certain similarities are found between the approach developed in detail here, and that mentioned in previous works.[42,43]

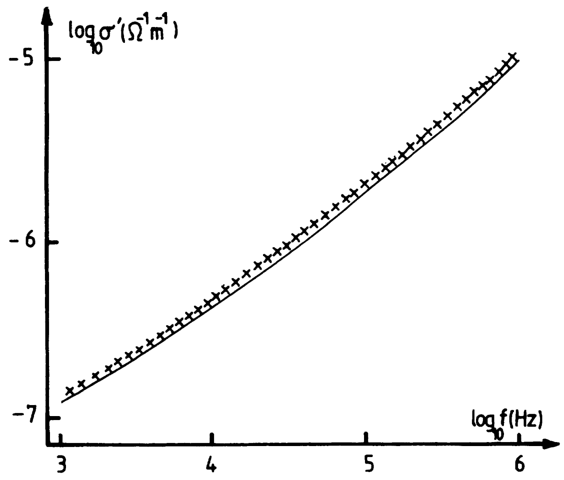

FIG. 6. Comparison between the polarization conductivity measured by impedance spectroscopy and calculated from the TSDC results. The solid line represents the calculated curve (slightly shifted to make the figure clearer).

They showed that the ion motion can be studied by the TSPC/TSDC method and by the dielectric losses (polarization conductivity). However it is necessary to take into account the specificity of both methods of measurement: one is performed when the sample is maintained at thermal equilibrium, the other proceeds by a programming of temperature.

Several studies[37,41,44] have underlined the consequences of this programming on the determination of the temperature of the observed phenomena. We supposed then that it was possible to assume a linear behavior in an attempt to establish a connection between both kinds of measurement.

If we call T_e the equilibrium temperature characterizing the experiments performed by complex impedance spectroscopy, and T the temperature characterizing the thermally stimulated currents, we thus supposed that, as commonly used[37]

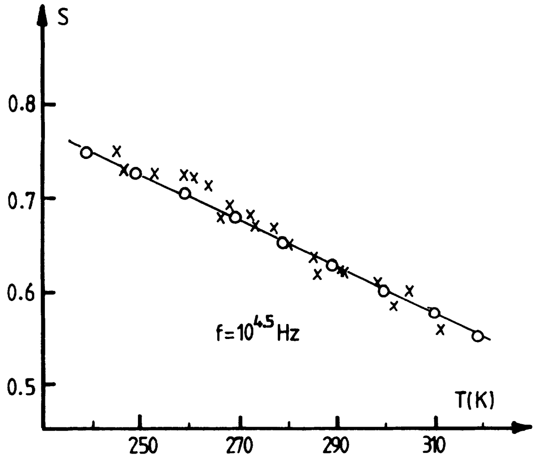

FIG. 7. Temperature dependence of parameter s. (×) experimental results (○) calculated by introducing the TSDC results.

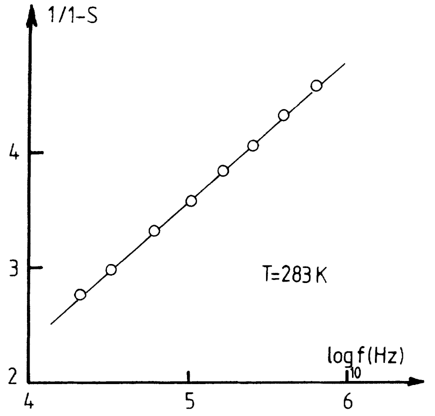

FIG. 8. Variation of1/1$-s$ as a function of the logarithm of frequency.

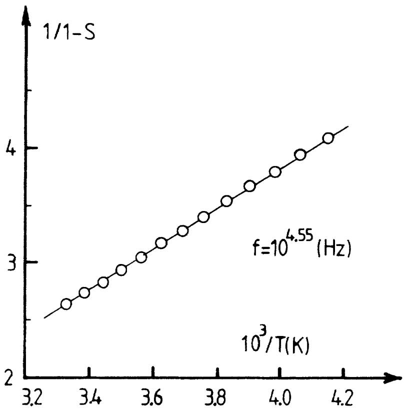

FIG. 9. Variation of 1/1$-s$ as a function of the inverse of temperature.

$$T_e - \alpha T = T_0 ,$$

where T_0 is a temperature close to that at which the observed phenomenon in TSDC commences. After this adjustment we have compared the results obtained by measuring the values of the polarization conductivity directly with the values calculated from the results obtained by determining the thermally stimulated currents. As an example, a comparison is represented in Fig. 6.

Obviously the most significant parameter obtained from the experiments is the exponent s. Any comparison would have been lacking in significance if it was shown unable to account for the evolution of the exponent.

In Fig. 7, we plotted the experimental points obtained on a glass, Na_2O-$3SiO_2$, and the points calculated, as we have already outlined, from the measurements of the thermally stimulated currents. This figure shows that there is good agreement between the two approaches. To our knowledge it is the first time that the evolution of an exponent s of the law, $\sigma'(\omega) = A\omega^s$, determined experimentally, is obtained by the way of a calculation based on a series of experiences of a different nature. Therefore the study of parameter s, and especially its physical signification, can be fruitfully undertaken by the use of the modified form [Eq. (3)].

For example the quantity $1/(1-s) = f(\ln\omega)$ should be a straight line. The results reported in Fig. 8 show as an example that it is the case, at $T = 283$ K. The slope is proportional to $1/\gamma$. In the same way, a plot of $1/(1-s) = f(1/T)$ gives a straight line, the slope being $W_e/\gamma k$ and the value obtained at the cross with the ordinates is η/γ (Fig. 9).

V. CONCLUSION

The polarization phenomenon has been studied, and the corresponding current has been ascribed to bound charges moving over short distances, on an atomic scale. Consequently a description of a sample in terms of a distribution of polarization is equivalent to its representation as a population of bound charges. Therefore we attempted, in a first approach, to show that the concept of "bound charge" could be used for all solids studied whatever the nature of the charge carrier. In the case of ionic conductors, the fluctuations near an equilibrium state create ionic movements on a microscopic scale, satisfactorily explaining the results. The generalization of the concept of "bound charge" seems a good view of the phenomena, when we consider in general the movements of the ions in ionically conducting glasses. This means that it is possible to determine the presence of bound charges when it is possible to measure a polarization conductivity. This led us to propose a generalization of the use of the universal law $\sigma'(\omega) = A\omega^s$.

This representation gives a physical significance to the exponent s, which appears as an evaluation of the ratio of the thermal movement of the charge carriers to the energies required to trap them in their sites. In this way conductivity measurements present a new interest and can give quantitative information on the dynamics of ions in ionically conducting glasses.

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