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Dynamic transport in ionic conductors

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The experimental data for the dielectric response of certain ionically conducting ceramics obtained by Kuhn and coworkers were re-interpreted using the "universal" dielectric formalism and the results reveal the presence of two well defined processes with power law exponents of -0.6 to -0.7 for the high-temperature, low-frequency branch and -0.3 and less for the low-temperature, high-frequency branch. The physical significance of these results is discussed in terms of transport in strongly anisotropic materials. © *1998 Kluwer Academic Publishers*

1. Introduction

The electrical and other properties of ionically conducting ceramics of composition $Na_{x-\delta}Fe_xTi_{2-x}O_4$, with $x = 0.875$, modified by soft chemistry extraction methods, to reduce the Na concentration with $0 \leqslant \delta \leqslant 0.44$, were studied in considerable detail by Kuhn *et al.* [1] who also included data of the frequency dependence of transport parameters.

In the present paper we are giving further detailed analysis of their dielectric data, using the "universal" dielectric response approach [2, 3] with a view to obtaining a better appreciation of the dynamics of ionic transport. We do this not only out of interest in the particular materials in question, but also from a more general standpoint, since we believe these data illustrate several points relevant to dynamic transport in ionic conductors.

In particular, we note the fact that in many situations the frequency dependence of the complex dielectric susceptibility

$$\tilde{\chi}(\omega) = \tilde{\varepsilon}(\omega) - \varepsilon_\infty = \chi'(\omega) - i\chi''(\omega) \propto (i\omega)^{n-1} \quad (1)$$

follows the "universal" fractional power law, where ω is the angular frequency, ε_∞ is the "high-frequency" permittivity beyond which the losses become negligible, the exponent falls in the range $0 < n < 1$, and Kramers–Kronig (KK) compatibility requires that

$$\chi''(\omega)/\chi'(\omega) = \cot(n\pi/2) \quad (2)$$

This means that logarithmic plots of $\chi''(\omega)$ and $\chi'(\omega)$ are parallel straight lines with slopes $n - 1$. The alternating current conductivity is given by $\sigma'(\omega) = \varepsilon_0\omega\chi''(\omega)$. We note that it is not *necessary* for the universal law to be applicable in all cases, but that where it appears not to be followed it is useful to try first removing certain obvious processes, like ε_∞, the direct-current (d.c.) conductivity, σ_0; any low-frequency dispersion (LFD) [3, 4], which follows the same laws, Equation 1 and 2, but with a very small value of n; and also any dipolar processes that may be present. At the end of this analysis it is often possible to obtain good self-consistent fractional power-law trends underlying the behaviour and this leads to a better analysis of the physical processes involved.

2. Experimental procedure

Of the samples referred to in this paper, NFT2 is the parent sample, the others having Na extracted by chemical means, with the following parameters

NFT2 has $x = 0.875$, $\delta = 0$, giving $x - \delta = 0.875$ for Na content

NFT3 has $x = 0.875$, $\delta = 0.2$ giving $x - \delta = 0.675$

NFT4 has $x = 0.875$, $\delta = 0.3$ giving $x - \delta = 0.375$

NFT5 has $x = 0.875$, $\delta = 0.03$ giving $x - \delta = 0.845$

These samples were prepared from finely ground powders by cold pressing into the form of pellets 5 mm in diameter and 0.3 mm in thickness, with silver painted contacts.

These materials are "fast ionic conductors" in that their structure contains unidirectional double channels along which Na^+ ions move relatively freely [1] and obvious limitations to free transport arise from structural imperfections and the finite size of the grains in the ceramic.

3. Results

We begin this presentation with two of the results of the removal of secondary processes for the parent sample NFT2, which correspond to extreme forms of response. Fig. 1 gives the result for 250 °C, where a Debye process is at 4×10^4 Hz. The two dotted lines have exponents $1 - n = 0.67$, which correspond to relatively dispersive regimes. The corresponding data for the lower temperatures of 82 and 135 °C are

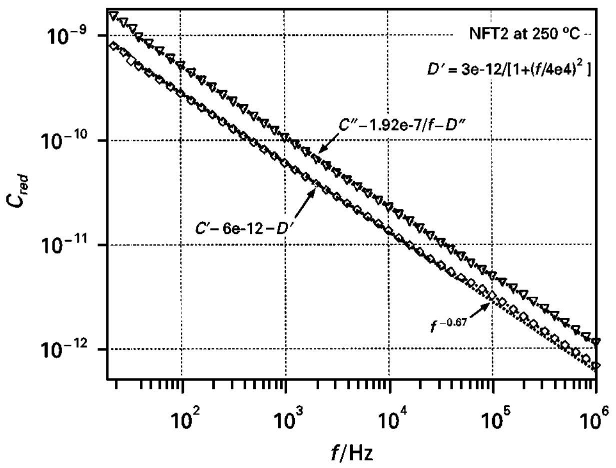

Figure 1 The reduced capacitance for NFT2 at 250 °C obtained from the raw data by subtracting the elements indicated, specifically C_∞, the d.c. component and a high-frequency Debye process, *D*. Also shown are the Kramers–Kronig compatible power laws with exponent − 0.67, to show the quality of the fit.

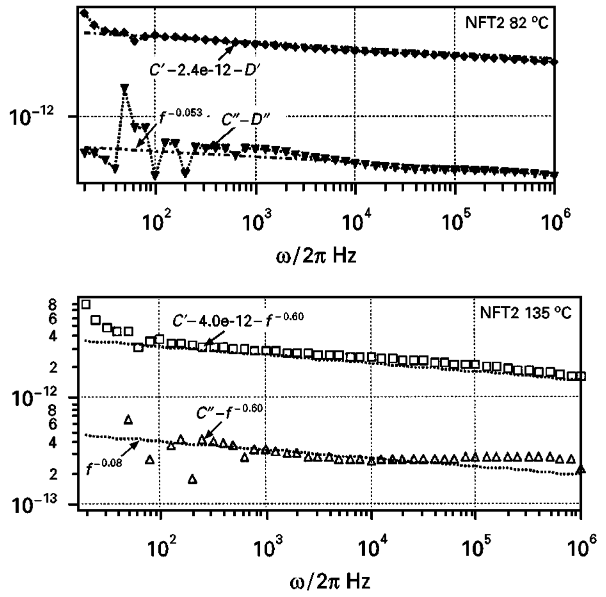

Figure 2 Comparable data to those of Fig. 1 corresponding to 82 and 135 °C, showing a very low-loss residual response, after subtraction of C_∞ and of a Debye process at 50 Hz. No d.c. was involved at these low temperatures. There is some noise in the loss component at low frequencies and a rise of the real part cannot be eliminated by ordinary means.

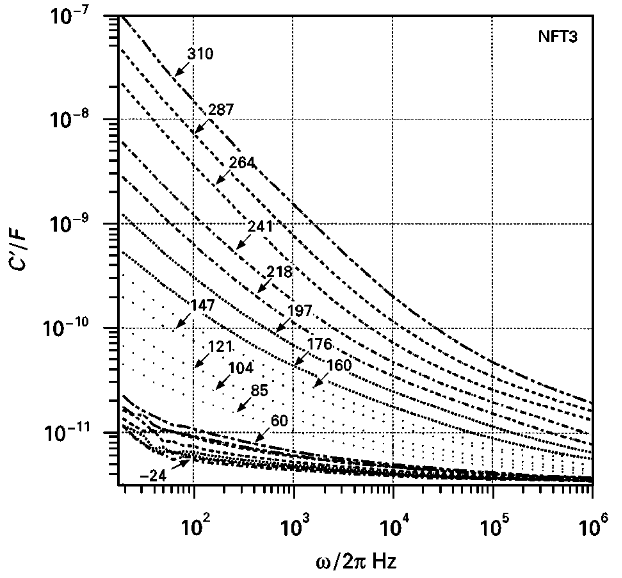

Figure 3 The complete set of raw data for the real part of the complex capacitance of sample NET3 showing increasing dispersion at lower frequencies with the temperature rising above 85 °C. Note the continuous curvature of the plots.

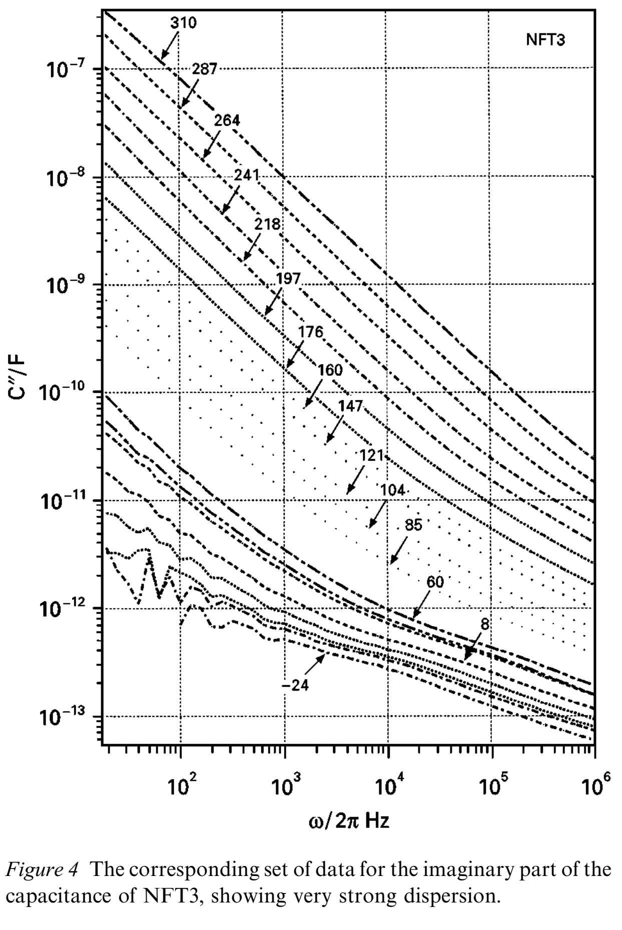

Figure 4 The corresponding set of data for the imaginary part of the capacitance of NFT3, showing very strong dispersion.

shown in Fig. 2, where a much lower loss behaviour is evident with an exponent $1 - n = 0.053$.

The remaining data for this sample leave much to be desired, in that it is not possible to obtain similar good fits because of the perturbing influences that cannot be eliminated satisfactorily, although data were recorded of the values of the various parameters and will be presented later.

Much more satisfactory fitting of data was obtained for sample NFT3 and we present in Figs 3 and 4 the complete raw data for this sample, so as to give a comparison with the reduced data presented in Figs 5 and 6 for two temperature ranges. We note continuous curvature of $C'(\omega)$ and $C''(\omega)$, which makes it impossible to define a single slope except at the lowest and highest temperatures. Fig. 5 gives the results of subtracting named elements, such as C_∞, d.c. and/or LFD at higher temperatures and also dipolar elements at low temperatures, giving good KK compatible power laws over more than four decades of frequency, with some irregularities at the lowest frequencies.

Fig. 6 gives the corresponding data for higher temperatures, with a predominance of strongly dispersive

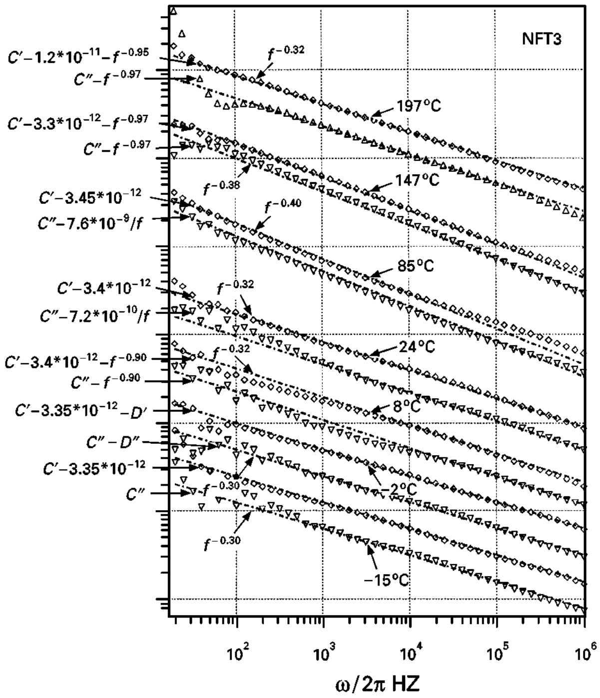

Figure 5 The residual dielectric response of sample NFT3 at a range of lower temperatures. The secondary processes subtracted are indicated in the tags on the margin, the figure following C' being C_∞, that following C'' being either in the form G_0/f for the d.c. contribution or f^{n-1} for the LFD elements. The Debye components are denoted by D' and D''. Points correspond to the reduced data, lines are the fitted power laws, which are drawn in KK compatible positions, the high-frequency exponents being indicated for every pair of data. In the interests of clarity each consecutive set of data is displaced with respect to the previous one by $10^{1/2}$.

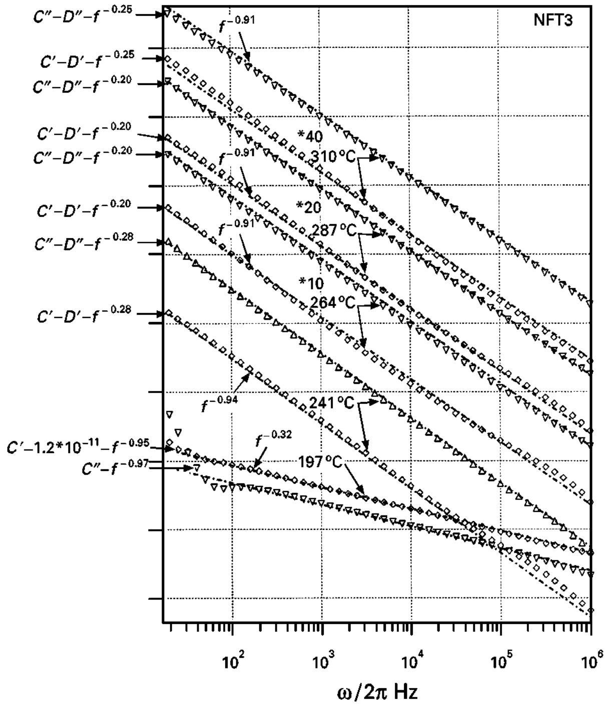

Figure 6 The corresponding higher temperature data, comparable to those shown in Fig. 3, but with the 197 °C set reproduced to provide a reference. The multiplying factors for data from 264 °C onwards are indicated by numbers.

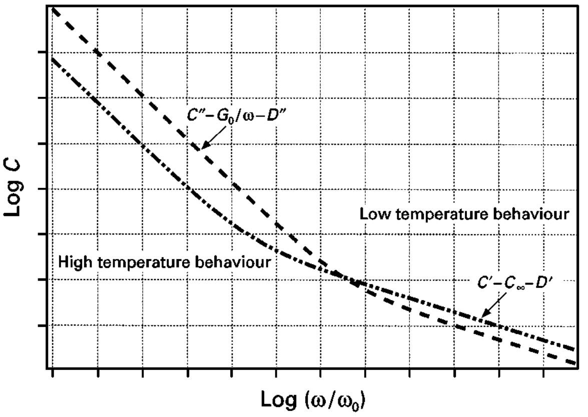

Figure 7 The calculated response given by Equation 1 over an extended frequency range with $1 - n_{\text{lf}} = 0.95$ and $1 - n_{\text{hf}} = 0.4$, showing the two branches corresponding to NFT3. The cross-over point between them is moving with temperature leading to the low- and high-temperature responses shown in Figs 5 and 6. The response for NFT2 would be almost constant at higher frequencies.

behaviour, including also the 197 °C data for comparison. The difference between the data in Figs 5 and 6 is more apparent than real, since the data consist of two components, which overlap to a large extent, as shown schematically in Fig. 7, and the derivation of the reduced data in Figs 5 and 6 correspons to the elimination of the less dominant element. The important point is that our procedure shows the power-law nature of the frequency dependence in both regions, extending in all cases right across the available frequency range and therefore presumably also well beyond that range, something that would not have been evident from the raw data in Figs 3 and 4.

The temperature dependence of the reduced loss is shown in Fig. 8 for selected frequencies between 25 and 1×10^6 Hz; showing good activated behaviour with an energy of 0.22 eV up to 197 °C and much more rapid temperature dependence for the more strongly frequency dependent behaviour. The fact that activation of the reduced loss is so regular suggests that we are dealing here with a more "elementary" process than could have been expected from the complex behaviour of the raw data.

Fig. 9 gives the frequency dependence of the reduced capacitance for sample NFT5, which is less heavily extracted than sample NFT3, shown in Figs 5 and 6. The "universal" trend is clearly visible, but the transition between the low- and high-temperature response is less gradual. There is also a clear tendency for the "diffusive" slope, $n = 0.5$, to dominate at low or high frequencies and manifest itself by coincidence of the real and imaginary components.

Fig. 10 gives the temperature dependence of $C' - C_\infty$ for all samples; in most cases the capacitance varies over two orders of magnitude. We have checked the impedance plot for sample NFT5 at the highest temperature and there is no indication of any series capacitive effect, which would be expected if barrier capacitances were responsible for the phenomena observed. The magnitude of the total loss, C'', at any frequency follows closely that of $C' - C_\infty$, confirming that they represent the same volume transport process. This is further confirmed by the recent finding that the response of these materials remains linear over a variation of signal amplitude by two orders of magnitude [5].

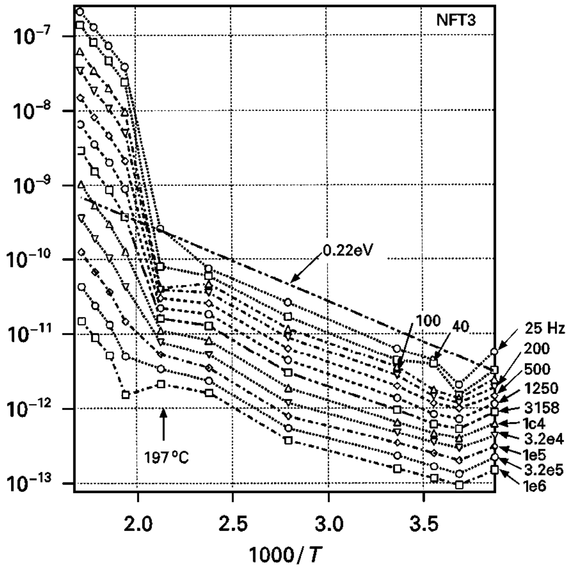

Figure 8 Activation plot of the reduced loss shown in Figs 5 and 6 with a well defined activation energy of 0.2 eV at all frequencies extending to temperatures up to 197 °C, indicated by an arrow, with a rapid growth of slope towards higher temperatures. Note that 197 °C is the highest temperature at which the "shallow" high-frequency power law in Fig. 5 is applicable.

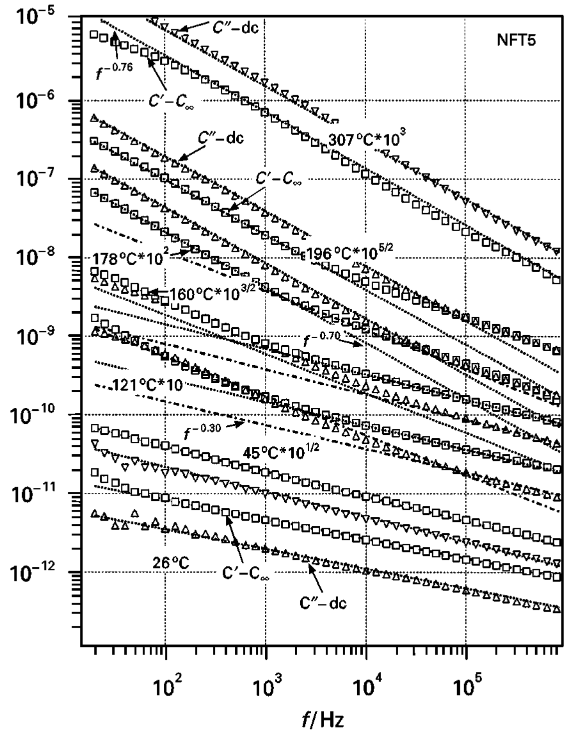

Figure 9 The residual responsse of the sample NFT5 showing features that are broadly similar to those of NFT2 in Figs 5 and 6, but with a less gradual transition from a strongly dispersive to weakly dispersive regime. The consecutive sets for the various temperatures are shifted vertically by the factors indicated. There is an evident tendency to $n = 0.5$ at intermediate temperatures dominating either at low frequencies, as at 121 and 160 °C, or at high frequencies, as at 178 and 196 °C.

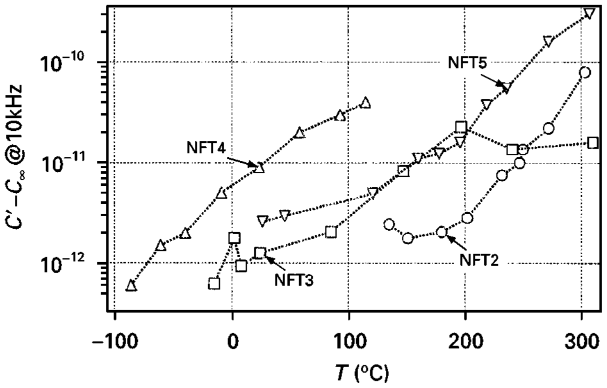

Figure 10 The temperature dependence of the active capacitance, C'–C_∞. The least extracted, sample 2, has the lowest, the most heavily extracted, sample 4, has the highest active capacitance.

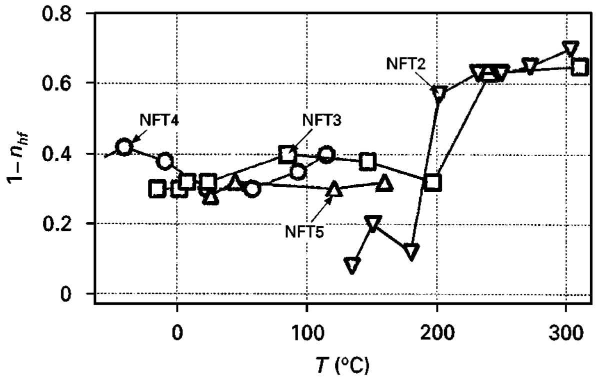

Figure 11 The temperature dependence of the high-frequency power law exponent, $1 - n_{\rm hf}$, shows two ranges: at high temperatures there is LFD-like behaviour going over below 180 °C into a virtually temperature-independent behaviour in which NFT3, 4 and 5 have similar values between 0.3 and 0.4, while NFT2 falls below 0.1.

The temperature dependence of the high-frequency exponent $1 - n_{\rm hf}$, is shown in Fig. 11. We note that above approximately 180 °C there is a rapid rise towards LFD-like values, while at lower temperatures the response is independent of temperature. However, it should be noted that neither very low values nor values close to one are seen.

4. Discussion

Our analysis of the experimental data for all four samples with different degrees of Na extraction leads to certain general conclusions, which may be summarized as follows

1. In all samples there exist two power laws with low- and high-frequency exponents, $n_{\rm lf}$ and $n_{\rm hf}$, which are relatively weakly dependent on temperature in their respective ranges. The analysis of data shown in Figs 5 and 6 proves that power laws of the type given in Equation 1, which combine to give the overall behaviour in Figs 3 and 4, are separately applicable over the entire available temperature range. This proves that these correspond to well defined separate physical processes, which give two very different values of exponents $n_{\rm hf}$ and $n_{\rm lf}$, neither of which is either very close to unity, corresponding to very low loss, or very low, corresponding to LFD. The transitions in temperature between the two exponents

are not equally easily observable: in some cases the transition is more rapid than in others.

2. The magnitude of the effective dielectric susceptibility, $C' - C_\infty$, at any given frequency is related to the degree of Na extraction, suggesting that the response is due to the density of free sites. On the other hand, the exponent of the power law does not depend significantly on the degree of extraction.

3. It is evident that the derivation of the reduced responses produces a much more plausible result, implying a simple but distinct physical processes at low and high frequencies. These processers are "universal" in terms of their fractional power law behaviour and we ask what constitutes the most plausible physical mechanism.

4.1. Physical mechanisms

A number of physical processes have been proposed to explain the universal behavior, among them the theories of Dissado and Hill [6] and of Weron and coworker [7, 8]; both of which refer specifically to dipolar processes, although it could be argued that they might be applicable to charge carrier transport, which this one evidently is.

There exist a number of theories dealing specifically with charge carrier systems [9–14], but it is very difficult to be specific in determining which of these may be applicable to our particular situation. Some of them do not give simple fractional power laws, which our data appear to confirm in reasonable detail.

For the present we do not propose to decide between these or other specific theoretical interpretations, since in our opinion this is not justified by the experimental situation. Instead we propose to discuss the physical significance of the generalized plot in Fig. 7, which clearly shows the division of the frequency range into two separate regions, characterized by distinctly different exponents. The immediate implication of the results derived here is that there exist two "modes" of alternating field transport in these samples, one of which is connected with a significantly higher loss per reversal of polarization than the other. The respective ratios are

$$X''(\omega)/X'(\omega) = \cot(n\ \pi/2) =$$

0.73 at low temperatures and high frequencies

and

12.7 at high temperatures and low frequencies

The ratio of 12.7 corresponds to a fairly conducting mode, with little energy stored, while the ratio 0.73 is close to the critical value of one, corresponding to classical diffusive behaviour [2], for which the stored and lost energies are equal.

This brings us to the physical significance of the frequency-independent ratio given by Equation 1, which is at the basis of the "energy criterion" [2, 3]. According to this approach, the power law, Equation 1, inevitably entails a frequency-independent ratio of energy lost per radian, W_l, to energy stored at the peak, W_s, which is given by

$$W_l/W_s = X''(\omega)/\tau'(\omega) = \cot(n\pi/2) \qquad (3)$$

The implication of a large ratio, Equation 3, is that the process is highly lossy and corresponds to LFD and we have little storage of energy, conversely a small ratio corresponds to a nearly perfect dielectric with very low losses and large storage. Processes related to low-loss dielectrics have low ratios, Equation 3 since most of the energy is stored electrostatically in the electric field and losses are relatively trivial; LFD processes which resemble normal d.c. transport are relatively very lossy, since the amount of energy stored is small. It is highly significant, however, that our analysis points to the existence of *both* LFD and d.c. in our samples and the full significance of this is not yet clear – in particular we do not know what mechanisms may be responsible for the storage of energy involved.

Conventional theoretical analysis derives the delay involved in polarization processes in dielectric response, assuming implicitly that the energy loss is the *consequence* of the delay, whereas the energy criterion analysis derives the energy lost and stored in the reveresal of polarization and obtains the frequency dependence from Kramers–Kronig relations. This approach was shown to be applicable to at least some specific situations such as the spectral response of semiconductor trapping processes [15] and LFD [16] and there is some evidence that the response of low-loss ferroelectrics belongs to the same category [17].

5. Conclusions

Our analysis shows that the two processes coexisting in our samples are independent of one another and there is little correlation between them; the only question is which of the two happens to be dominant at any particular temperature and frequency. Given that the two transport regimes at low and high temperatures both follow the universal law with low and high losses, respectively, it is interesting to speculate on the nature of the physical processes determining those losses. We are dealing with ceramics, *i.e.* polycrystalline materials, which in each crystallite have an "easy" direction of flow along the natural channels, and 'difficult" directions normal to that. However, the "easy" paths do not extend all the way along the macroscopic single crystals, since lattice defects interrupt the flow and charge carriers have to follow more difficult paths. We may therefore postulate the existence of two types of transport: easy transitions within finite lengths of channels, determining the high-frequency behaviour, and the more difficult transport within and between the individual single crystal grains separated by intergrain barriers, determining the more lossy low-frequency response. A more detailed analysis showing how fractional power laws are obtained in these two cases is presented in the accompanying paper [18].

With regard to the temperature dependence of the two processes, the low-frequency process involves transport over large energy barriers, which must give rise to strong thermal activation. By contrast, the easy transport along preferred directions does not involve any significant energy loss and the temperature dependence is relatively weak.

This argument explains, therefore, the main features of the experimental observations.

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