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Dielectric Response of Materials: Extension to the Debye Model

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Abstract

The Debye model is frequently used to explain the dielectric behaviour of materials. A good description of the experimental results is often obtained by using a distribution of relaxation times. In this work, it is proposed to extend the Debye model to the depolarisation of two or more types of dipoles occurring simultaneously. With this procedure, it is observed that permittivity Cole–Cole plots appear with two or more semicircles overlapping each other, and can give origin to one flattened semicircle. The same type of behaviour is observed for the impedance Cole–Cole plots, and both type of description of experimental data usually give very similar results. Assuming that relaxation times are thermally activated parameters, with positive or negative activation energies depending on the type of the dipoles, it is possible to obtain dielectric responses similar to those of the paraelectric regions of ferroelectric materials, and dielectric peaks on the permittivity-versus-temperature graphs similar to the relaxor behaviour found in some ferroelectric materials. © 1999 Elsevier Science Limited. All rights reserved

Keywords: Debye model, dielectric properties, electrical properties, ferroelectric properties.

1 Introduction

The dielectric behaviour of materials under an external ac applied field has been the focus of numerous papers, in view of its high scientific and technologic importance. Measurements are made in a very wide range of frequencies and temperatures, and for many types of materials. Jonscher[1] made a very comprehensive review on the subject, and presented a model, the many-body model, for the dielectric spectroscopy.[2] This model introduces the idea of correlated states in the material, arising from interactions between individual dipoles in an interactive system, which form a narrow half-filled band. The preferred orientations of the system can be represented by two potential wells, where their relative occupancy determines the total polarisation, and the application of the external field will excite these states making transitions between the two wells. The authors proposed three types of transitions, one of them, denoted *a*, corresponding to the classical thermally-excited transition of a single particle from one well to the other, which is the case involved in the Debye process.[1] The other two transitions *correspond to configurational tunnelling in which large number of interacting particles undergo small adjustments which collectively give the result of a large transition of a single particle (sic)*. The results of this model agree with many experimental data, since it gives an expression similar to the 'Universal' law, i.e. the experimental observation that the depolarisation current $i(t)$ has a power-law dependence on t, $i(t) \propto t^{-n}$. It is also significant that near the loss peak frequency, the model gives a Debye-like behaviour. However, it is well known that the ideal Debye model do not describe the dielectric response of the majority of the materials, and other approaches have been made to this model, namely, the assumption that the dipoles have a distribution of relaxation times. Since the many-body model predicts a region near the loss peak where the Debye description is observed, it would be interesting to check if a system with two or more types of dipoles, i.e. dipoles with different relaxation times, described by the Debye model, would give a dielectric behaviour similar to those experimentally found. This case is different from the ones considering a distribution of relaxation times, since we are not looking for any specific distribution in only one process, but rather to different processes with specific relaxation times.

2 Basic Concept

Figure 1 represents the frequency variation of the real and the imaginary parts of the complex

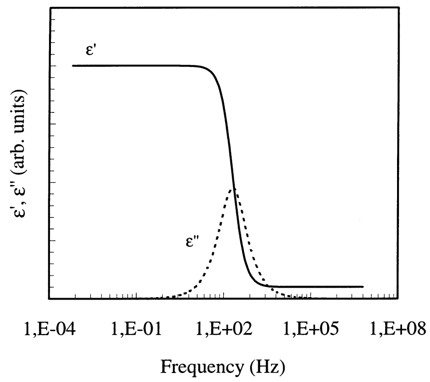

Fig. 1. Sketch of the frequency variation of the real and imaginary parts of the complex relative permittivity of a material.

relative permittivity, hereafter designated simply by ε' and ε'', respectively, of an arbitrary material. In the high frequency region, ε_∞ consists of the free space contribution and of the sum of all dielectric susceptibilities for the mechanisms operating in the material, and, in the low frequency region, ε_s consists in ε_∞ plus the relaxation mechanism corresponding to the loss peak region. We need to find an expression of the form

$$\varepsilon(w)' = \varepsilon_\infty + f(w) \tag{1}$$

which reduces to $f(0) = \varepsilon_s - \varepsilon_\infty$, for $w = 0$. When a steady field is switched off, following Debye, the polarisation decays exponentially with a time constant τ, the characteristic relaxation time of the dipole, as

$$P(t) = P_{\mathrm{O}} e^{-t/\tau} \tag{2}$$

To obtain the frequency response $f(w)$, we take the Laplace's transform,

$$f(w) = \int_0^\infty P(t) e^{iwt} \mathrm{d}t = \frac{P_{\mathrm{O}}}{-iw + 1/\tau} \tag{3}$$

Using the condition $f(w)$ for $w = 0$, we obtain the known Debye equation

$$\varepsilon(w)' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{-iw\tau + 1} \tag{4}$$

which, after the separation of the real and imaginary parts, gives

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (w\tau)^2} \tag{5}$$

$$\varepsilon'' = \frac{w\tau(\varepsilon_s - \varepsilon_\infty)}{1 + (w\tau)^2} \tag{5'}$$

In this paper we shall use the same concept of depolarisation current that gave origin to eqn (5′), but with two or more types of dipoles. If the system has n different types of dipoles, the solution for eqn (3) is simply

$$f(w) = \sum_{j=1}^{n} \frac{P_j \tau_j (1 + iw\tau_j)}{1 + (w\tau_j)^2} \tag{6}$$

where P_j is the contribution of the dipole type j to the polarisation, and hence

$$\sum_{i=1}^{n} P_j = P_{\mathrm{O}} \tag{7}$$

With eqn (7) and the condition $f(0) = \varepsilon_s - \varepsilon_\infty$, the substitution of eqn (6) into eqn (1) will give the desired Debye description with many types of dipoles. Equation (6) is therefore an extension to the Debye model, taking in consideration the simultaneous depolarisation of dipoles with different relaxation times. We are now able to compute some arbitrary parameters in order to check if the proposed extension is adequate to the analysis of experimental data.

3 The Simplest Case: Two Types of Dipoles

The simplest case is, of course, when $j = 2$. We shall assume that $P_1 = \beta P_{\mathrm{O}}$, and $P_2 = (1 - \beta) P_{\mathrm{O}}$, where β is the fraction of P_{O} due to P_1. The solutions for the real and the imaginary parts are then,

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{\beta\tau_1 + (1 - \beta)\tau_2} \left(\frac{\beta\tau_1}{1 + (w\tau_1)^2} + \frac{(1 - \beta)\tau_2}{1 + (w\tau_2)^2} \right) \tag{8}$$

$$\varepsilon'' = \frac{\varepsilon_s - \varepsilon_\infty}{\beta\tau_1 + (1 - \beta)\tau_2} \left(\frac{\beta\tau_1^2}{1 + (w\tau_1)^2} + \frac{(1 - \beta)\tau_2^2}{1 + (w\tau_2)^2} \right) \tag{8'}$$

which reduce to eqn (5) and (5′), respectively, for $\beta = 1$ (or $\beta = 0$), as expected.

We shall first analyse different cases, assuming any arbitrate values for ε_s and ε_∞, at constant temperature, i.e. with τ_1 and τ_2 constants. Figure 2

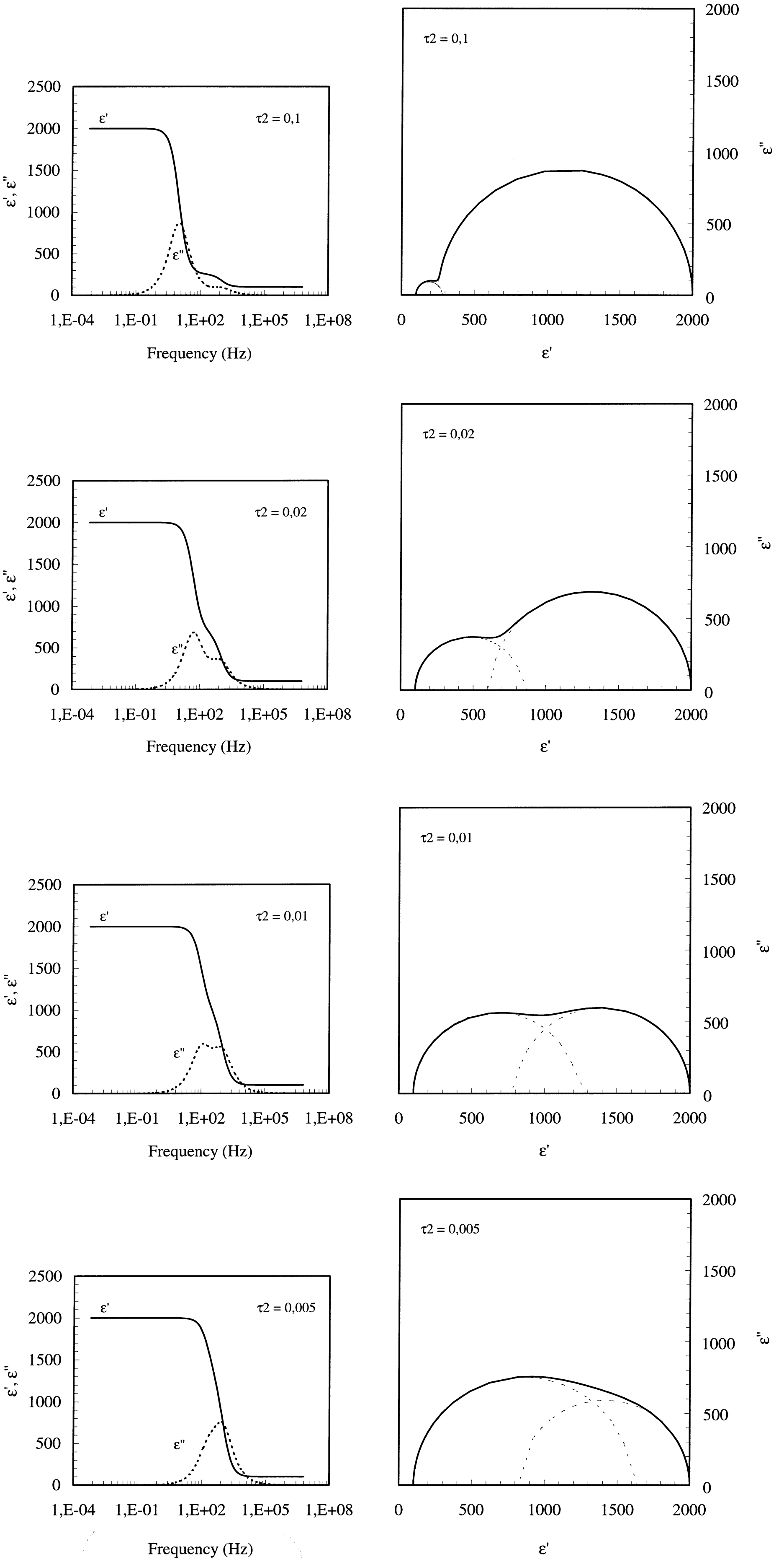

Fig. 2. Variation of ε' and ε'' with frequency (left column) and Cole–Cole plots of the complex permittivity, ε'-versus-ε'' (right column), for four different values of the relaxation time τ_2 (inserted in each case), keeping constant $\beta = 0{\cdot}9$ and $\tau_1 = 0{\cdot}001$ s. The values of ε_s and ε_∞ can be arbitrarily chosen, but in these examples they are 2000 and 100, respectively.

shows the variation of ε' and ε'' with the frequency, in the left column, and the Cole–Cole plot, ε' – versus – ε'', in the right column, for fixed values of β, $\beta = 0\cdot 9$, and $\tau_1 = 0\cdot 001$, and for four values of τ_2. It can be seen that, when the two relaxation times, τ_1 and τ_2, are closer to each other, the loss peaks (ε''-versus-frequency) merge together and give 'one' rounded, non-Debye type, loss peak, and the relaxation regions (ε'-versus-frequency) also become a non-Debye type relaxation region. This means that we do not need a distribution of relaxation times within only one process, in order to describe the experimental results like the one presented in Fig. 2, but, instead, two or more types of dipoles each one with its own relaxation time described by the same time function as those proposed by Debye to fit the data. Far from the loss peaks, either for lower or higher frequencies, the dielectric loss depends on w^{+1} and on w^{-1}, respectively, as expected for the Debye model, and cannot explain other observed frequency dependencies, as pointed out by Jonscher.[1] The Cole–Cole plots show two semicircles with relative positions in the ε' scale depending on the difference between τ_1 and τ_2: for a large difference, the two semicircles intersect slightly, while, for a low difference, they are almost coincident. In the last example of Fig. 2, the plot seems like a flattened semicircle, or a semicircle centred below the ε' axis, which is the case normally taken as non-Debye with a distribution of relaxation times.

Knowing the variation of ε' and ε'' with frequency, it will be important to see their effect on the impedance spectroscopy of the material. We introduce here the dc conductivity, σ_{dc}, which we assume constant throughout the frequency spectrum, i.e. it does not interfere with the dipoles. This should be the case of a homogeneous and resistive material, since we are omitting other types of polarisation, namely the Maxwell–Wagner relaxation behaviour. Assuming that ε' is the permittivity value of a perfect capacitance and ε'' the conductivity of a resistance, with $\sigma_{ac} = w\varepsilon_0\varepsilon''$, any dipole will function as an RC parallel element, because the same voltage is applied to both elements. The equivalent circuit of such a case is the one shown in Fig. 3. Figure 4(a) gives the impedance Cole–Cole plot of this circuit, in the case where there is only one dipole (we assumed a geometric factor $g = A/l = 1$, where A is the electrode area and l is the length of the material). It can be seen that the system shows three minima for Z'': one for low frequency (high Z' value), which corresponds to the dc conductivity of the material; another one at intermediate frequencies, which is observed at the frequency of the maximum of ε'', i.e. the Debye frequency of the dipole; and the last one at high frequency (low Z' value), which depends on both ε_s and ε_∞. The intermediate Z'' minimum is more or less pronounced depending on the ε_∞ value: the lower the ε_∞ value the lower the Z'' value; this minimum never touches the Z' axis, and, consequently, the two semicircles will always

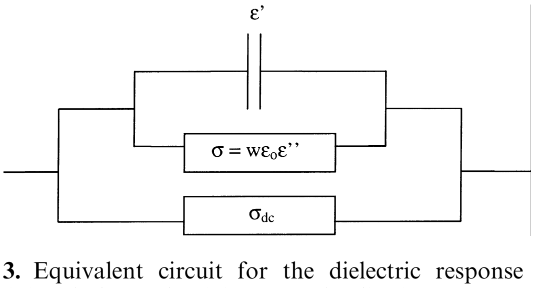

Fig. 3. Equivalent circuit for the dielectric response of a material with dc conductivity, σ_{dc}. The dipoles are assumed to contribute with a pure capacitive part, ε', and a resistive one, $\sigma_{ac} = w\varepsilon_0\varepsilon''$.

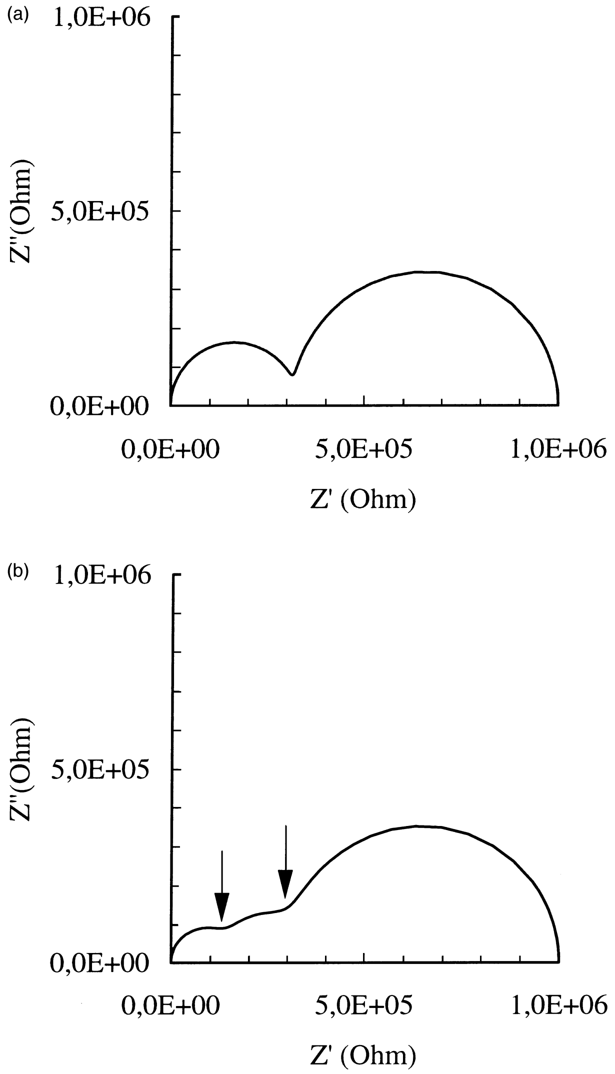

Fig. 4. Impedance Cole–Cole plots for the equivalent circuit of Fig. 3: (a) when only one type of dipole is present, with a relaxation time of $\tau_1 = 1\cdot 25 \times 10^{-3}$ s; (b) when two types of dipoles are present, with τ_1 as before, $\tau_2 = 8.(3) \times 10^{-5}$ s, and $\beta = 0\cdot 4$ (the arrows indicate the two relative minima for Z''). The geometrical factor $g = A/l$ (A = area of the electrodes, l = length of the material) is taken as $g = 1$ m, and $\sigma_{dc} = 1 \times 10^{-6}$ (Sm^{-1}). For the dipoles, it was assumed $\varepsilon_s = 300$, and $\varepsilon_\infty = 10$.

intersect each other. Figure 4(b) gives again the impedance Cole–Cole plot, but now with two types of dipoles. The choice of the parameters used was made to conveniently see a fourth Z'' minimum [marked with an arrow in Fig. 4(b)], which appears in the Debye frequency of the new dipole. This type of plots are seen in many experimental cases (e.g. Ref. 3). In Fig. 4(a) and (b) we wanted to show that impedance Cole–Cole plots can be used to separate the contributions from dc and ac components, in one part, and to separate the contributions of different dipoles, in the other. However, it must be emphasised that careful microstructure analysis and experimental design must be performed in the material, in order to separate the contributions of other 'accidents', like porosity, second phases, grain boundaries, and electrodes.[4,5]

4 The Effect of the Temperature

If the temperature is changed we shall expect it to influence the polarisation of the dipoles. Two cases are possible: (i) for higher temperatures it will be more difficult to orient the dipoles by the applied field due to the thermal agitation energy, and (ii) the higher the temperature the higher the density of dipoles available contributing to the total polarisation. The first case can be treated by a Langevin type equation, which leads to a variation of the dielectric susceptibility, $\chi' = \varepsilon' - 1$, proportional to $1/T$. If the material suffers any phase transition, the equation can be rewritten with a correction parameter, T_O, giving the well known Curie–Weiss law, where $\chi' \propto 1/(T - T_O)$. It is conceivable that this behaviour corresponds to an increase in the relaxation time for a given type of dipoles, i.e. the higher the temperature the slower the polarisation process. This is normally formulated by an activation process for the relaxation time, of the type

$$\tau = \tau_0 \exp(-U/kT) \tag{9}$$

where U is the energy to orient the dipoles, and can be related to the viscosity of the dielectric medium. In the second case, the dielectric susceptibility must increase with the increase of the temperature, since the density of the dipoles is now increasing. Making the same approach as before, this could be seen as a faster polarisation process, since the probability of a charge of one sign to find nearby a charge of opposite sign in order to make a dipole will be higher. Thus, eqn (9) can be used with a negative U energy.

The two cases pointed should have physical meaning. In the first one, the dipoles are thought as independent entities, i.e. not interacting with each other, and correspond to the Debye model, e.g. induced electronic dipoles. It is also assumed that their density stays constant with temperature. The second case is normally observed in glass systems and in ceramic materials, and is assigned to ionic jumps, where both the density and the jump frequency increase with temperature; again, non interacting dipoles are assumed. The change in the density of the dipoles should influence the low frequency region of the permittivity spectrum, i.e. the ε_s value should change with temperature, while for the high frequency region, ε_∞ should be almost independent of the temperature, since we can assume that electronic and ionic polarisabilities are the only ones present. We shall analyse the cases where both ε_s and ε_∞ are constant with temperature, since any variation of these values should be taken from the experiments.

In Fig. 5 the solid line corresponds to the case where there is only one type of dipole in the material, with a positive activation energy for the relaxation time [case (i) above]. This is an expected plot because, if the relaxation time is increasing with temperature, the relaxation process will disappear at some high temperature. The interesting feature of the graph is that it shows a similar behaviour for the temperature–permittivity dependence observed in some perovskite type materials, such as $SrTiO_3$ and $KTaO_3$, which follows the quantum-mechanical formula proposed by Barrett.[6] In Fig. 5 the equation here proposed, is plotted with the values for M, T_1, and T_0, of the

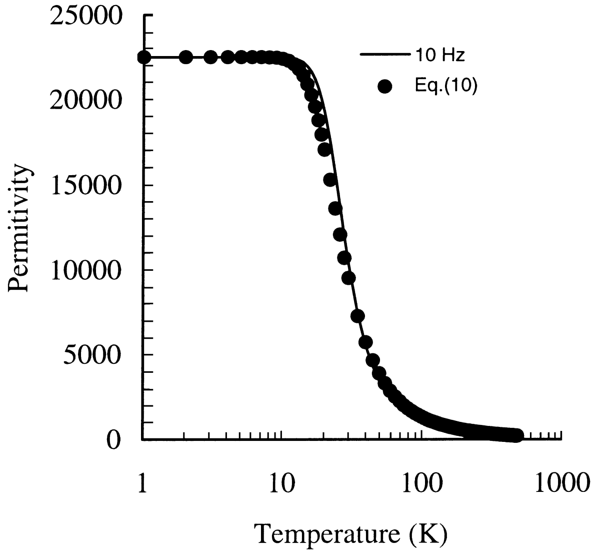

Fig. 5. Variation of the real part of the dielectric permittivity, ε', in the case when there is only one dipole in the material. The relaxation time changes with the temperature [eqn (9)] with $\tau_O = 0{\cdot}12\,s$, and $U = -0.005$ eV. The solid line corresponds to the variation of the permittivity at 10 Hz. The points correspond to eqn (10) with $M = 9 \times 10^4$ K, $T_O = 38$ K, and $T_1 = 84$ K.

following eqn (10), determined for the $SrTiO_3$ system:[7]

$$\kappa = \frac{M}{\frac{1}{2}T_1\coth(T_1/2T) - T_O} \qquad (10)$$

where κ is the permittivity. In this figure, the agreement of eqn (10) with the plot for the 10 Hz frequency dependence of the permittivity using the Debye model is very good (it is possible, of course, to adjust the τ_O and U values in order to obtain a similar result for any other frequency). Since eqn (10) turns to be of the Curie–Weiss type for high temperature, it can thus be assumed that the approach taken above for case (i) is valid, i.e. that the temperature dependence of the relaxation time, eqn (9), is applicable to the Debye model. The agreement between the two curves in Fig. 5 is formally expected from the mathematical point of view, since for high temperatures both depend exponentially on the temperature. However, they significantly differ on the physical basis. Equation (10) is derived for the ionic polarisability of the Ti ions in titanates, for temperatures above the Curie point, i.e. for the nonferroelectric state. Here, we assumed that the ionic polarisability do not change much with temperature (it contributes to both ε_s, and ε_∞), and we are only analysing the decrease of ε_s, to ε_∞ i.e., the effect of the temperature on the relaxation behaviour of some unknown dipole. If this dipole is assumed to be originated from the Ti ions in the perovskite titanates, which follow the Debye relaxation with the relaxation time depending on the temperature with an energy of 0·005 eV (the value used in Fig. 5), then it will show a temperature $T_1 = 58\,K$, which is not far from the experimental value of $T_1 = 84\,K$. However, some care must be put in the above analysis, because the very high ε_s value at low temperature must be consistent with the ionic polarisability of the Ti ions.

Table 1. The parameters used in the calculations of ε'-versus-temperature in the case when two types of dipoles are present [eqn (8)]. For all examples, $\beta = 0{\cdot}999$

	$\tau_{O1}(s)$	$U_1(eV)$	$\tau_{O2}(s)$	$U_2(eV)$
Fig. 6	50	−0·2	0·1	−0·01
Fig. 7	50	−0·2	0·1	0·01
Fig. 8	1×10^{-9}	0·3	0·1	−0·02

If the energy U in eqn (9) is negative, one obtains a plot exactly opposite of that of Fig. 5. The next step is then to see what will happen if two types of dipoles are present in the material with relaxation times dependent on temperature, either with the same sign for the energy or with different ones. In Fig. 6 we plotted the case where both energies are negative with the rest of the parameters chosen in a way that it could originate another accident in the graphs (Table 1 lists the parameters used). The figure shows a peak in the permittivity after the first decrease shown in Fig. 5, where the temperature of the maximum of the permittivity, T_m, decreases with increasing frequency. The appearance of only one peak is observable in the case where the energy of one the dipoles is negative, Fig. 7 (parameters listed in Table 1), with the same behaviour for the T_m with frequency. When both the U energies are positive, or if the U energy for the faster process is positive and the other negative, one permittivity peak appears again, Fig. 8 (parameters listed in Table 1), but now with T_m increasing with increasing frequency. It can also be seen in Fig. 8 that the maximum of the permittivity

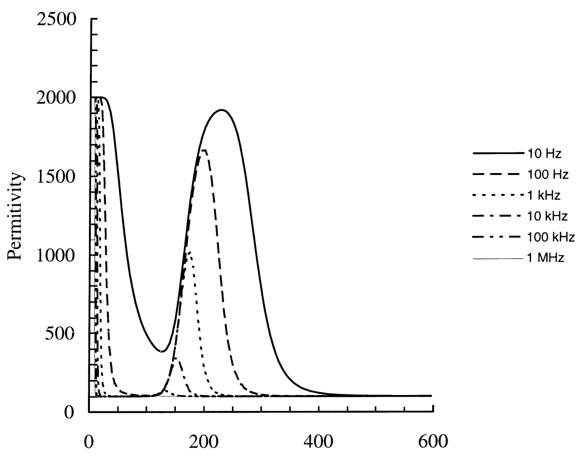

Fig. 6. Variation of the real part of the dielectric permittivity, ε', with temperature, for five frequencies, in the case when there are two dipoles in the material, both with positive energies for the relaxation time (parameters used in Table 1).

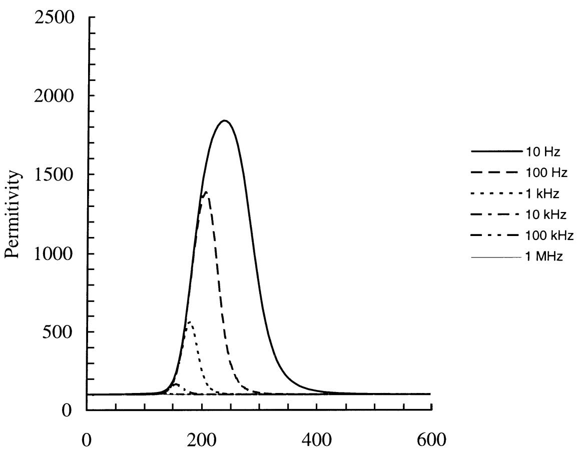

Fig. 7. Variation of the real part of the dielectric permittivity, ε', with temperature, for five frequencies, in the case when there are two dipoles in the material, one with positive energy and the other one with negative energy for the relaxation time (parameters used in Table 1).

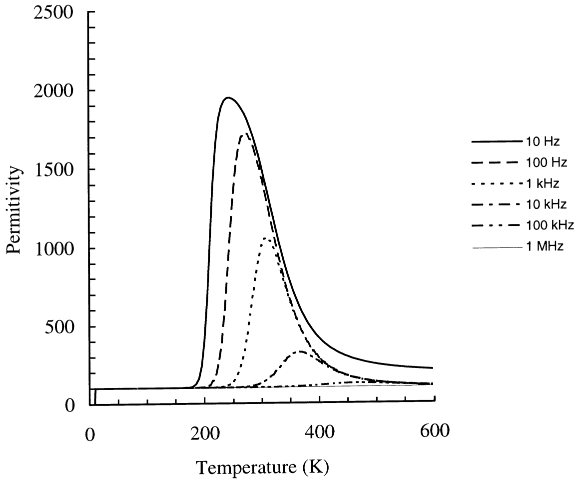

Fig. 8. Variation of the real part of the dielectric permittivity, ε', with temperature, for five frequencies, in the case when there are two dipoles in the material, one with positive energy and the other one with negative energy for the relaxation time (parameters used in Table 1). The results are similar to those observed in relaxor materials.

for a given frequency, ε_m, decreases with the increase of the frequency. The interesting feature in this figure is that it shows a permittivity peak very similar to that of the relaxor behaviour observed in some ferroelectric materials.[8] Using the Vögel–Fulcher relation, used to describe the relaxation in spin-glass systems,[8]

$$w = w_O \ \exp\left[-U_a/k\left(T_m - T_f\right)\right] \tag{11}$$

where T_m is the temperature of the maximum permittivity for the w frequency, and T_f is the static freezing temperature, with the values of Fig. 8, one obtains an activation energy U_a of 0·44 eV, which is far above the energies for the relaxation time used. Comparing this value with the one obtained by Viehland *et al.*[8] for the PMN-10PT system, 0·0407 eV, it can be seen that our calculations are unable to explain the relaxor behaviour of these systems. If the relaxor behaviour is explained by a spin-glass model, it means that the system is viewed as interacting superparaelectric clusters with size dispersion, and a relatively small difference in the clusters size would make a large change in their fluctuation frequency.[8] In this paper, we are not including in the model any interaction between the dipoles, and this could be the reason why the model fails to explain the relaxor behaviour in some materials. If the dipoles do not interact with each other, then it is possible to observe an experimental curve like the one shown in Fig. 8. This seems to be the case in $Bi_4Ti_30_{12}$ single crystals, which show a dielectric anomaly in the temperature range of 500 to 600°C, i.e. below the transition temperature, as reported by Kim *et al.*[9] A rough estimation of the activation energy using eqn (11) with the authors values (Fig. 3 in Ref. 9), gives 1·0 eV, which is in the energy range that the present model is able to explain.

5 Conclusions

In this paper we tried to extend the Debye model for the relaxation behaviour of dielectrics by including more than one dipole type, each one with its relaxation time. This is different from the case where one chooses a distribution of relaxation times for the same dipole. It was shown that the inclusion of more than one dipole type is enough to obtain Cole–Cole plots with overlapped semicircles or with flattened semicircles. Taking the temperature dependence for the relaxation times, it was also shown that, depending on the sign of the activation energies, it is possible to obtain peaks on the permittivity-versus-temperature graphs, some of them following the relaxor behaviour found in some ferroelectric materials.

It must be emphasised that the extension of the Debye model aims to explain experimental results sometimes found in ceramic materials, particularly in the frequency region where loss peaks are observed. For frequency regions far from this one, and as pointed out by Jonscher,[1] the experimental results are better described by other time functions rather than the exponential one. In the Debye model, the dipoles do not interact to each other, but perhaps the inclusion of retardation process in this model could account for the interaction between the dipoles. This is under study in order to analyse its effect also in the case of ferroelectric domain motion. The existence of permanent dipoles in piezoelectric materials and their effect on the relaxation process is of main scientific interest, and it was not taken in consideration in this paper. Both issues will be treated in a forthcoming paper.

In the design of experiments it is very important to pay attention to the physical state of the material, namely the electrodes, as pointed out by Fleig and Maier,[5] who showed, by finite-element study, that the impedance Cole–Cole plots can significantly change with the shape of porous electrodes. This parameter as well as other material parameters like second phases, interaction with atmosphere, and porosity, for example, must be taken into consideration in the analysis of experimental results. In this paper we took only the effect of different dipoles in the relaxation process, and not the effect of different resistivities that the materials can show. This issue emphasises the need to separate experimentally the current originating from the polarisation/depolarisation process from that of the electronic transport in the material.

Acknowledgements

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