ISSN 1541-308X, Physics of Wave Phenomena, 2014, Vol. 22, No. 4, pp. 262–265. © Allerton Press, Inc., 2014.

OPTICAL AND DIELECTRIC PROPERTIES OF SOLID MATERIALS OF BIOMOLECULES

Relaxation Dielectric Spectra in the Presence of Conductivity

G. I. Ovchinnikova[1*], A. P. Eremeev[1], I. Yu. Polyakova[1***], and A. A. Fomin[2****]**

[1] *Faculty of Physics, Lomonosov Moscow State University, Leninskie Gory 1/2, Moscow, 119991 Russia*

[2] *Faculty of Computational Mathematics and Cybernetics, Lomonosov Moscow State University, Leninskie Gory 1/52, Moscow, 119991 Russia*

Received June 8, 2014

Abstract—A concept of analyzing complex dielectric spectra under the assumption of a simultaneous contribution from two dispersion mechanisms to the dielectric response is proposed. It allows describing complex dielectric spectra of ferroelectrics and some conducting materials with unusual dispersions.

DOI: 10.3103/S1541308X14040098

1. INTRODUCTION

Dielectric spectra are usually analyzed within models associated with a particular type of material, when one mechanism can be well assumed to make a dominant contribution to the dielectric response. However, for certain conditions (temperature, phase transition) or materials (composites) it could be difficult to specify the response mechanisms and the corresponding models. This is especially true for the microwave range of dielectric spectra. For example, at temperatures close to the phase transition temperature, microwave dielectric spectra of ferroelectrics, which are dielectrics under normal conditions, considerably deviate from those typical of Debye-type dielectrics and can even demonstrate small negative permittivity values typical of the response of conducting materials [1] or a damped oscillator [2]. At the same time, solid electrolytes described by the Drude model with negative permittivity demonstrate the positive values typical of the dielectric response in microwave range [3].

In this work, we analyze dielectric spectra of materials with unusual dispersion using two dispersion mechanisms in the dielectric response, namely, the relaxation orientation mechanism typical of dielectrics and the conductivity-related mechanism.

2. THEORETICAL MODELS

In this work, the dielectric response of the orientation component is described by the Debye model of dipole rotation in a viscous medium where the dependence of the permittivity ε' on the frequency ω has the form

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon'(0) - \varepsilon_\infty}{1 + i\omega\tau_1}, \tag{1}$$

and the dielectric response of the conducting component, σ^*, is described by the Drude model of motion of charge carriers in a viscous medium:

$$\sigma^* = \frac{\sigma_0}{1 - i\omega\tau_2}. \tag{2}$$

In (1) and (2), $\varepsilon'(0)$ and ε_∞ are the static and high-frequency components of the permittivity, σ_0 is the frequency-independent conductivity, and τ_1 and τ_2 are, respectively, the Debye- and Drude-model relaxation times. The relationship between ε^* and σ^* is described by the classical expression

$$\varepsilon^* = -\frac{i\sigma^*}{\varepsilon_0\omega}. \tag{3}$$

Separating the real and imaginary parts, we obtain

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon'(0) - \varepsilon_\infty}{1 + \omega^2\tau_1^2} - \frac{\sigma_0\tau_2}{\varepsilon_0(1 + \omega^2\tau_2^2)}, \tag{4}$$

$$\varepsilon''(\omega) = \frac{[\varepsilon'(0) - \varepsilon_\infty]\omega\tau_1}{1 + \omega^2\tau_1^2} + \frac{\sigma_0}{\varepsilon_0\omega(1 + \omega^2\tau_2^2)}, \tag{5}$$

$$\sigma(\omega) = \frac{b\omega^2\tau_1}{1 + \omega^2\tau_1^2} + \frac{\sigma_0}{1 + \omega^2\tau_2^2}, \tag{6}$$

where $b = \varepsilon_0[\varepsilon'(0) - \varepsilon_\infty]$.

Formulas (4)–(6) allow spectra of different materials to be described by universally accepted characteristics, dielectric ε' and ε'' and conducting ε' and σ. As follows from (5) and (6), the characteristics that

*E-mail: gio@physics.msu.ru
**E-mail: ap.eremeev@physics.msu.ru
***E-mail: iy.polyakova@physics.msu.ru
****E-mail: xander.fomin@ya.ru

describe losses in both models are always positive at both low and high frequencies, and the competing contributions from the orientation and conducting components change the main spectrum in the low-frequency region for ε'' and in the high-frequency region for σ. As to the real part of the permittivity ε', there are two contributions with different signs, and ε' can be either positive or negative depending on the dominant contribution from the dielectric response.

Far from the dispersion regions ($\omega\tau < 1$), where the permittivity does not depend on the frequency, the sign of $\varepsilon'(\omega)$ will always be determined by the dominant contribution from the major dielectric response mechanism, and the small contribution from the minor mechanism, even with the opposite sign, will therefore be hard to observe if there is no other evidence for its presence. In the regions of strong dispersion ($\omega\tau \sim 1$), where the contribution from the major mechanism decreases with increasing frequency, the minor mechanism will manifest itself as a maximum or a minimum against the background of the insignificant contribution from the major dispersion mechanism. This takes place at certain relationships between the parameters $\varepsilon'(\omega)$ and σ_0 and between the relaxation times of the two mechanisms. These relationships are found from the roots of the biquadratic equation obtained by setting the derivative $d\varepsilon'/d\omega$ equal to zero:

$$\tau_2^3\tau_1^2(\sigma_0\tau_1^2 - \tau_2 b)\omega^4 + 2\tau_1^2\tau_2^2(\sigma_0\tau_2 - b)\omega^2 + \sigma_0\tau_2^3 - b\tau_1^2 = 0. \quad (7)$$

Out of four roots of equation (7), only two are real:

$$\omega_{1,2} = \sqrt{a_1 + a_2 \pm a_3}, \quad (8)$$

$$a_1 = \frac{\sigma_0}{b\tau_2 - \sigma_0\tau_1^2}, \quad a_2 = \frac{b}{b\tau_2^2 - \sigma_0\tau_2\tau_1^2},$$

$$a_3 = \frac{(\tau_1^2 - \tau_2^2)\sqrt{b\sigma_0\tau_2}}{\tau_1\tau_2^2(b\tau_2 - \sigma_0\tau_1^2)}.$$

As is evident from (8), ω_1 and ω_2 differ only by the sign of the third term in the radicand which is the very expression that is determined by the relationship of the relaxation times and the contributions from different response components. At fixed relaxation times, the frequency at the extremum point will increase or decrease depending on the relationship between the contributions from $\varepsilon'(0)$ and σ_0. In each case, there will be only one extremum, maximum or minimum, the form of which is determined by the second derivative

$$\frac{d^2\varepsilon'}{d\omega^2} = \frac{2\tau_1^2[\varepsilon'(0) - \varepsilon_\infty](3\omega^2\tau_1^2 - 1)}{(1 + \omega^2\tau_1^2)^3} + \frac{2\varepsilon_0\sigma_0\tau_2^3(\varepsilon_0 - 3\tau_2^2\varepsilon_0\omega^2)}{(\varepsilon_0 + \tau_2^2\varepsilon_0\omega^2)^3}. \quad (9)$$

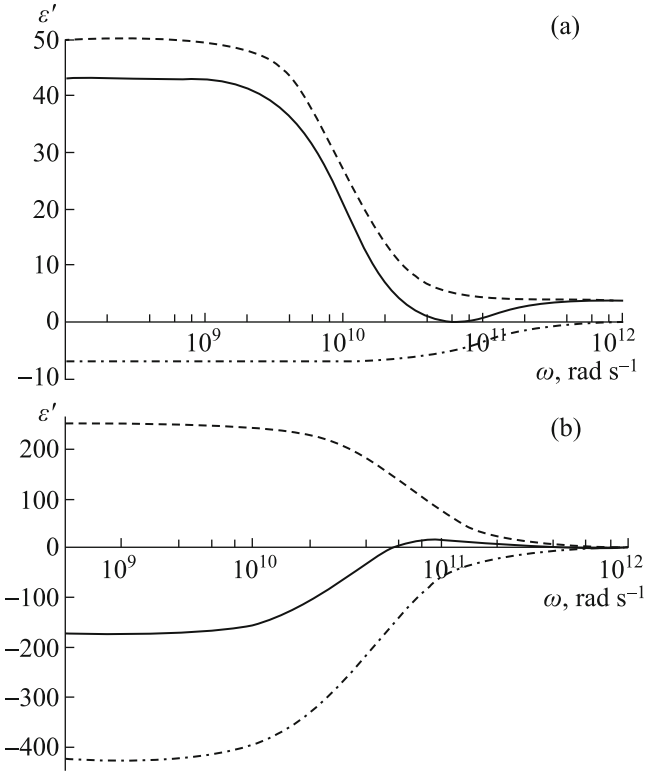

Fig. 1. Frequency dependence $\varepsilon'(\omega)$ of the Debye-model permittivity (dashed line), Drude-model permittivity (dot-dashed line), and total permittivity (solid line) for the parameters (a) $\tau_1 = 10^{-10}$ s, $\tau_2 = 10^{-11}$ s, $\varepsilon'(0) = 50$, and $\sigma_0 = 6\,(\Omega\,\mathrm{m})^{-1}$; (b) $\tau_1 = 1.5\times10^{-11}$ s, $\tau_2 = 2.5\times10^{-11}$ s, $\varepsilon'(0) = 250$, and $\sigma_0 = 150\,(\Omega\,\mathrm{m})^{-1}$.

As an example, we consider frequency dependences of the real part of the permittivity for the cases where the dominant contribution comes from the Debye component (Fig. 1(a)) or from the conducting component (Fig. 1(b)). In each case, the values of the Debye model and Drude model parameters were chosen in accordance with the data from [1, 2]. The curves calculated by formula (4) for both cases will be referred to as the total spectrum.

It is evident from Fig. 1 that by choosing parameters $\varepsilon'(0)$, ε_∞, σ_0, τ_1, and τ_2 we can obtain dielectric spectra with the domination of the Debye-type response and Drude-type spectra in which the high-frequency dispersion regions show a dielectric response unusual for each of the models. In the Debye model, the permittivity cannot fall below the level of ε_∞, and in the Drude model it cannot be positive. Note that in both cases the contribution from the minor dielectric response mechanism only slightly changes the total spectra in the dispersion-free region, and it cannot be observed unless there is additional evidence for its presence in another region of the spectrum, i.e., in the dispersion region.

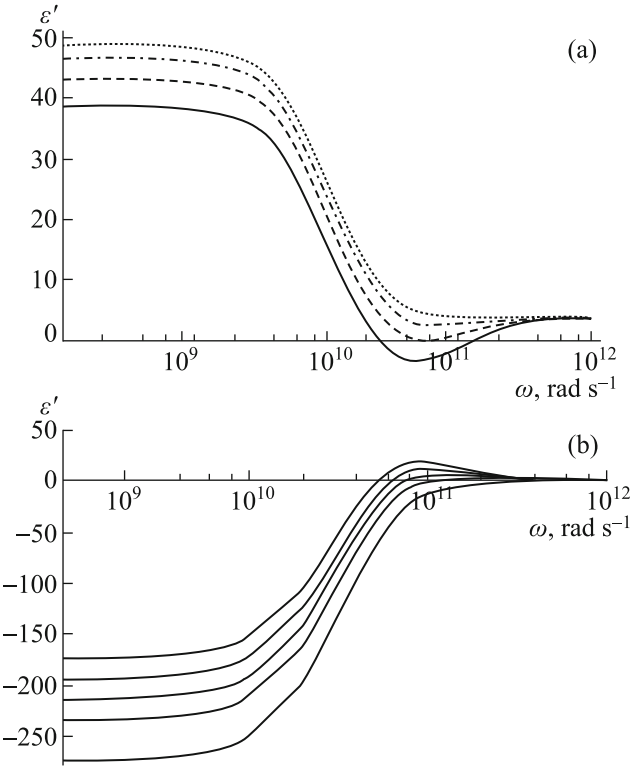

Fig. 2. Frequency dependence of the total permittivity $\varepsilon'(\omega)$ for the parameters (a) $\tau_1 = 10^{-10}$ s, $\tau_2 = 10^{-11}$ s, $\varepsilon'(0) = 50$, and (from top to bottom) $\sigma_0 = 1$, 3, 6, and $10\,(\Omega\,\mathrm{m})^{-1}$; (b) $\tau_1 = 1.5\times10^{-11}$ s, $\tau_2 = 2.5\times10^{-11}$ s, $\sigma_0 = 150\,(\Omega\,\mathrm{m})^{-1}$, and (from bottom to top) $\varepsilon'(0) = 150$, 190, 210, 230, and 250.

The spectra in Fig. 1 are calculated for the microwave range, where ε_∞ has the lowest value easily exceeded even by a small contribution of the other sign to the dielectric response from the minor mechanism, which makes the total dielectric response fundamentally different. In the low-frequency dispersion regions, ε_∞ is determined by the response of the higher-frequency relaxation dispersion and usually has a large value which can conceal the contribution from the minor mechanism. That is why ε'' or the loss tangent rather than ε' is chosen as the dielectric response observation parameter in the analysis of low-energy dielectric spectra [4, 5].

Figure 2 shows a family of total dielectric spectra the parameter of which is the conductivity σ_0 if the Debye contribution dominates (Fig. 2(a)) and the static permittivity $\varepsilon'(0)$ if the Drude mechanism contribution dominates (Fig. 2(b)). It is seen that as the conductivity increases, the total dielectric spectrum is transformed in the dispersion region from the Debye spectrum to the spectrum in which permittivity at high frequencies decreases below ε_∞ and even becomes negative. Spectra similar to the total spectrum in Fig. 1(a) and to the spectra in Fig. 2(a) are exhibited by some of ferroelectrics [1, 4]. Interestingly, the behavior of the same ferroelectrics in the measurements performed at different laboratories corresponds to one of the four curves in Fig. 2(a).

If the response of the conducting component dominates, the increase in $\varepsilon'(0)$ transforms the Drude spectrum with negative $\varepsilon'(\omega)$ to the spectrum in which $\varepsilon'(\omega)$ becomes positive at high frequencies. Similar spectra are exhibited by some of solid electrolytes [3].

Losses in dielectric spectra are usually analyzed using the representation of these spectra as a frequency dependence of the imaginary or real parts of conductivity. These curves calculated by formulas (5) and (6) are shown in Fig. 3. It is seen that the increase in the conductivity in the frequency dependences of ε'' changes the Debye response in the low-frequency region (on the left of $\varepsilon''_{\max}$) while the increase in the permittivity in the Drude-type response is observed in the high-frequency region. The dependences in Fig. 3 are similar to those in [4, 5] for low frequencies.

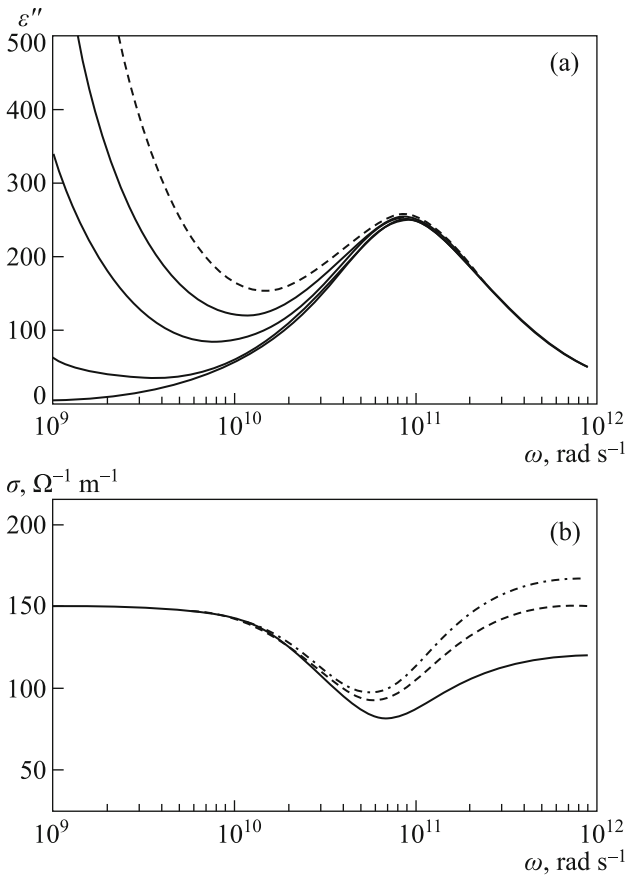

Fig. 3. Frequency dependences $\varepsilon''(\omega)$ and $\sigma(\omega)$ for the parameters (a) $\tau_1 = 10^{-10}$ s, $\tau_2 = 10^{-11}$ s, $\varepsilon'(0) = 50$, and (from bottom to top) $\sigma_0 = 0.5$, 3, 6, and $10\,(\Omega\,\mathrm{m})^{-1}$; (b) $\tau_1 = 1.5\times10^{-11}$ s, $\tau_2 = 2.5\times10^{-11}$ s, $\sigma_0 = 150\,(\Omega\,\mathrm{m})^{-1}$, and (from bottom to top) $\varepsilon'(0) = 150$, 190, and 210.

As to the conductivity σ, it decreases with increasing frequency, as the Drude model predicts, but after reaching the minimum it begins increasing again, which is unusual for the response of conducting systems. Similar dependences $\sigma(\omega)$ together with the dependence $\varepsilon'(\omega)$ (Fig. 2(b)) are observed in a number of solid electrolytes [3]. Moreover, as in the case of ferroelectrics, the spectra exhibit a great variety of dielectric responses [6].

3. CONCLUSIONS

A new approach is proposed for analyzing dielectric spectra of materials whose dielectric response shows dispersion unusual for them. These are dielectrics with spectra deviating from the pure Debye shape and solid electrolytes with dielectric spectra deviating from the Drude dependence. Dielectrics exhibiting this behavior are, for example, ferroelectrics near the phase transition temperature. Now there are a lot of experimental data on microwave dielectric dispersion of ferroelectrics that indicate typical features in their dielectric spectra.

First, they mainly follow the Debye model but deviate from it on approaching the phase transition temperature. Second, when approaching the phase transition, they exhibit an increase in the relaxation time if their spectra are analyzed using only the Debye model. The first feature is now described by various modifications of the Debye equation and by introducing the relaxation time distribution, which does not help understand mechanisms of the processes. The second feature is ascribed to increasing in the relaxation time on approach to the phase transition temperature, the mechanism of which is usually not specified.

The proposed concept of analysis of dielectric spectra of ferroelectrics under the assumption of the simultaneous contribution from two relaxation mechanisms to the dielectric response of those materials allows the dielectric dispersion mechanisms to be explained by the understandable physical processes accompanying the restructuring of the domain structure.

As to the materials with the dominant dielectric response of the conducting type, e.g., solid electrolytes, their Debye-model component can be due to a change in the solvate shell of the ions participating in the conductivity, which should introduce the Debye component to the dielectric response [7]. In this case, the proposed model also allows spectra to be analyzed on the basis of understandable physical mechanisms.

The proposed model appears to be applicable to the description and analysis of spectra of a wider range of materials exhibiting both conducting and dielectric properties, i.e., composite materials.

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