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Low-frequency dielectric spectroscopy of ferroelectric liquid crystals: near-electrode and bulk processes

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Frequency dependences of complex permittivity components have been studied in the 10^{-3} to 10^{5} Hz frequency range at temperatures of 310 to 370 K for a ferroelectric liquid crystals (FELC) both in the pure state and doped with strongly and weakly dissociating admixtures. Two dispersion regions have been revealed. The higher-frequency dispersion region I has been shown to be observed is smectic phases only. The average relaxation time is 0.7 ms and depends slightly on the impurity presence. The dispersion region II is observed in all phases of planar-oriented FELC and its parameters are heavily impurity-depending. The latter dispersion region has been shown to be due to local molecular orientation change in the near-electrode region having a thickness equal to the Debye shielding length. The "blurred" relaxation time in smectic phases has been supposed to be caused by the complex process of the molecular orientation change including both change in the smectic tilt angle and a partial rotation about the helicoid axis.

В интервале частот 10^{-3}–10^{5} Гц и температур 310–370 К исследованы частотные зависимости компонент комплексной диэлектрической проницаемости сегнетоэлектрического жидкого кристалла (СЖК) как в чистом виде, так и с добавлением сильно и слабо диссоциирующих примесей. Найдено две области дисперсии. Показано, что более высокочастотная область дисперсии I наблюдается только в смектических фазах. Время релаксации составляет в среднем 0,7 мс и слабо зависит от наличия примесей. Область дисперсии II наблюдается во всех фазах планарно ориентированного СЖК. На ее параметры существенно влияет наличие примесей. Показано, что данная область дисперсии обусловлена локальным изменением ориентации молекул в приэлектродной области, толщина которой равна дебаевской длине экранирования. Сделано предположение, что причиной "размытого" времени релаксации в смектических фазах может быть сложный процесс изменения ориентации молекул, включающий как изменение смектического угла наклона, так и частичное вращение вокруг оси геликоида.

It was shown first in [1] for various dielectric liquids and nematic liquid crystals (LC) that the low-frequency dielectric spectroscopy can be used as an effective method for investigation of the electrode/liquid crystal interface. Further studies made it possible to define the processes resulting in that the electric field in the sample becomes inhomogeneous under certain frequencies. Such processes include the charge exchange at the electrode/liquid interface [2]; ionic polarization of the sample [3, 4]; and the local changes of molecular orientation in the near-electrode region [5, 6]. Under a substantial influence of such phenomena, the relaxation process parameters measured at low frequencies can characterize mainly the near-electrode properties of LC but not bulk material ones.

It is known [7–12] that some specific low-frequency dispersion regions may manifest themselves in dielectric spectra of ferroelectric liquid crystals (FELC). These regions are related both to changes of the molecular tilt angle in the smectic layer (soft mode) [8, 10] and to the molecule rotation about the helicoid axis (Goldstone mode) [11, 12]. Such modes may have a relatively low frequency. Therefore, not only a frequency overlap between the bulk and surface relaxation processes may be possible but also a presentation of the processes caused by surface phenomena as the bulk ones. When considering the publications aimed at studies of such FELC dielectric spectra, it can be concluded that the main aim of essentially all those works was to define what mode corresponds to a specific relaxation process. The possible appearance of dispersion regions due to near-electrode processes was not taken into account in essence.

Therefore, the main purpose of this work is to determine the overlap extent of bulk low-frequency relaxation processes with surface ones and how those can mutually influence.

The study object was a mixture of 4-*p*-hexyloxyphenyl-4-*p*-octyloxybenzoate and 4-*p*-hexyloxyphenyl-4-*p*-decyloxybenzoate (62.3 and 31.2 % by mass, respectively) containing a polar chiral admixture LUCH-15 (6.5 % by mass). This FELC has the following phase states and phase transition temperatures:

$$\mathrm{I}\ 358\ \mathrm{N}^*\ 349\ \mathrm{SmA}\ 345\ \mathrm{SmC}^*\ 313\ \mathrm{C}.$$

Both pure FELC and that doped with strongly and weakly dissociating impurities were studied. The D_1 and D_2 dyes were used as the weakly dissociating dopants. The structure formulas of dyes are presented in Fig. 1. The dye concentration in the FELC was 1.1 to 1.2 % by mass. Tetrabutylammonium iodide (TI) (0.4 % by mass) was used as the strongly dissociating dopant. The polarization microscopy has shown that neither weakly dissociating impurities nor the strongly dissociating one (in the above concentrations) influence essentially the phase states and phase transition temperatures.

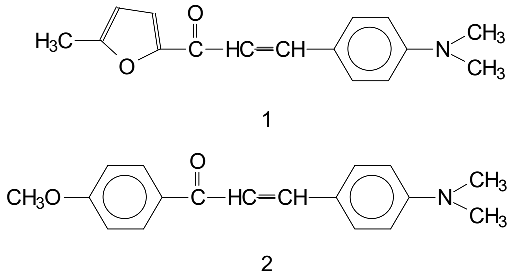

Fig. 1. Structure of D_1 (1) and D_2 (2) dyes.

The planar sample orientation was set by rubbed polyimide. The samples used in the study had the sandwich structure. The FELC thickness, d, was set within limits of 20 to 60 μm. The measurements were made mainly on the $d = 20$ μm samples. The polarization microscopy has shown that within such sample thickness range, the perfect homogeneous homeotropic or planar orientation are attained only for the chiral nematic (N^*) phase. Smectic phases (SmA, SmC^*) were not oriented in a strictly homogeneous fashion.

As in [1], the capacity C and resistance R in the 10^{-3} to 10^5 Hz frequency range were measured using oscilloscopic technique [13] in the parallel substitution scheme. The triangular measuring voltage pulse amplitude U_0 was varied within limits of 0.1 through 1 V. The measurements were made mainly at $U_0 = 0.25$ V. The temperature was stabilized to within 0.2 K using a home-made thermostat with low electromagnetic noise level.

From the measured C and R values, the complex permittivity components ε' and ε'' were determined using the known cell geometric parameters. Fig. 2 presents the frequency dependences of ε'' for the SmC^* phase of planar-oriented pure FELC (1), FELC+1.1 % D_1 (2), FELC+0.4 % TI (3) as well as for homeotropically oriented pure FELC (4) (measurements were made at temperatures presented in Table 1). It is seen that for all samples, there is an ε'' maximum near $f = 300$ Hz (the dispersion region I). Consideration of experimental $\varepsilon''(\varepsilon')$ dependences (Cole-Cole diagrams) has shown that, independent of the FELC orientation and impurity presence, those can be approximated by half-circles, that is, described mathematically basing on the Debye equation

$$\varepsilon_1^* = \varepsilon_{\infty 1} + \frac{\varepsilon_{s1} - \varepsilon_{\infty 1}}{1 + i\omega\tau_l}, \qquad (1)$$

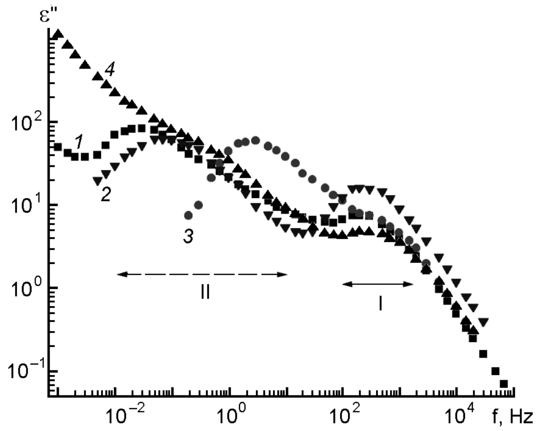

Fig. 2. Frequency dependences of ε'' for planar-oriented pure FELC (1), FELC+1.1 % D_1 (2), FELC+0.4 % TI (3), and homeotropic-oriented pure FELC (4). The measuring temperatures see Table 1. The sample thickness d = 20 μm.

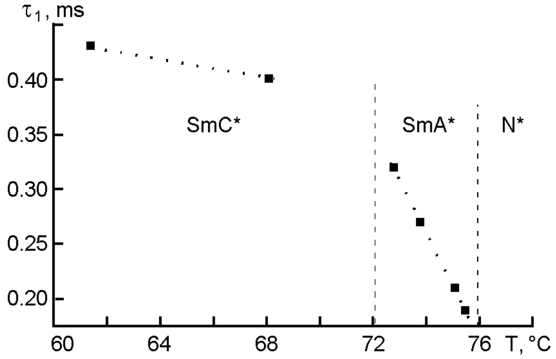

Fig. 3. Temperature dependence of τ_1 near the SmC*–SmA phase transition for planar-oriented FELC+1.1 % D_1. The sample thickness d = 20 μm.

where ε_1^* is the complex permittivity; ε_{s1} and $\varepsilon_{\infty 1}$, the permittivity values for $f = \infty$ and $f = 0$, respectively; τ_1, the dielectric relaxation time. In Table 1, presented are the τ_1 values for FELC at different molecular orientations and impurity concentrations. It follows from the data obtained that there is no substantial distinctions in τ_1 for different samples (the differences do not exceed 25 % of the average value).

It is to note that the dispersion region I is observed only in SmA and SmC* phases of the FELC. It is just the temperature dependence of τ_1 near the SmA–SmC* phase transition [7–10] that is of most importance for explanation of the formation mechanism of the above-mentioned region. Fig. 3 shows that dependence for the FELC+1.1 % D_1. It follows from these data that τ_1 increases as the temperature approaches the T_C value characteristic for the transition mentioned. According to [7–10], this relaxation process answers to the soft mode and is described as

$$\tau_1 = \frac{a}{T - T_c}, \tag{2}$$

where a is a factor. For the data presented in Fig. 3, a = 2 kHz/K. This value is almost one decimal order lower as compared to those obtained for many others FELC [7–10] that may be due to the very narrow range of the SmA phase and to a strong effect of the N*–SmA phase transition. It follows also from the Fig. 3 that the τ_1 values for SmC* and SmA phases are very close together. The weak $\tau_1(T)$ dependence in the SmC* phase allows to suppose that in that phase, the relaxation process is due to the Goldstone mode.

The τ_1 was studied also as a function of the measuring voltage U_0. It follows from the Table 2 that the τ_1 value remains essentially the same as U_0 varies from 0.1 to 10 V. This fact evidences that the measuring signal is selected correctly, does not

Table 1. Dependence of parameters characterizing the low-frequency dispersion regions I and II on the FELC molecular orientation and the presence of strongly and weakly dissociating impurities therein

Sample No.	Orientation	T, K	τ_1, ms	τ_2, s	α_2	W, *muБV V#mB* m	σ_{DC} ($T \approx 350$ K), $\Omega^{-1} \cdot m^{-1}$
FELC	planar	313.2	0.81	8.8	0.38	0.32	$2.3 \cdot 10^{-8}$
FELC	homeotr.	313.5	0.59				$2.8 \cdot 10^{-8}$
FELC+1.1 D_1	planar	313.4	0.61	2.9	0.30	0.54	$1.5 \cdot 10^{-8}$
FELC+1.2 D_2	planar	313,9	0,63	2,5	0,32	0.60	$4.0 \cdot 10^{-8}$

cause the system saturation and is high enough to provide a good signal/noise ratio. Even the highest voltages from the above range were insufficient to suppress the Goldstone mode and reveal the soft one in SmC* against the Goldstone mode background. Therefore, the soft mode existence in the SmC* phase of the FELC studied is still unclear and requires a further study. Thus, the data obtained allow us to conclude that the dispersion region I in the SmA phase answers to the soft mode while in the SmC* phase, it is most likely the Goldstone mode.

Unlike the dispersion region I, the II one is observable in all phases of the planar oriented FELC, including the isotropic one. It follows from the Fig. 2 that there is no such low-frequency dispersion region at the homeotropic FELC orientation. The increase of ε'' seen in Fig. 2 is caused by relaxation process that is due to the tunneled charge exchange at the FELC/electrode interface. This relaxation kind is observable not only in planar-oriented FELC but in any liquid at all [1, 2] and is not related directly to the molecular orientation. Thus, its consideration is out of the frame of this work.

The Cole-Cole diagram analysis for the dispersion region II shows that for I and N* phases, those are of half-circular shape, thus, are described also by the relationship (1). For SmA and SmC* phases, the Cole-Cole diagrams are arc shaped. According to [1], this answers to the Cole-Cole dispersion

$$\varepsilon_2^* = \varepsilon_{\infty 2} + \frac{\varepsilon_{s2} - \varepsilon_{\infty 2}}{1 + (i\omega\tau_2)^{1-\alpha_2}}, \tag{3}$$

where α_2 is the Cole-Cole parameter.

Table 1 presents the parameters characterizing the dispersion region II for both pure FELC and for the material containing various dopants. The conductivity σ_{DC} data for those substances in the N* phase are also presented. The σ_{AC} value in SmC* phase cannot be compared, since, as is shown in [14], it is due not only to presence of ions but also to nonlinear electric properties of smectic phases. It follows from experimental data that the relaxation time τ_2 (the dispersion region II) depends on the impurity concentration in a more strong manner than τ_1 does. When comparing τ_2 with τ_{DC}, it is seen that these quantities are in approximately in inverse proportion to one another.

Table 2. The parameters characterizing the low-frequency dispersion regions I and II for the pure planar-oriented FELC on the measuring signal voltage U_0. $T = 342$ K (SmC*)

U_0, V	τ_1, ms	τ_2, s	α_2
0.10	0.74	0.41	0.38
0.25	0.74	0.41	0.38
0.50	0.75	0.40	0.37
1.00	1.02	0.38	0.32

Another substantial feature of the dispersion region II consists in high ε'' values attaining 10^2 in maximum, Fig. 2. It is to note that in the same frequency range, ε' is rather high, too. Since the high ε'' and ε' values are observed in I and N+ phases, this cannot be related to spontaneous polarization. It was supposed [1] that this is due to the fact that the field in the sample becomes inhomogeneous at such low frequencies. The main fraction of the field is applied to the near-electrode layer of the sample. To determine the thickness of that layer, W, let us assume (as in [1]) that the near-electrode layer parameters are the same at both electrodes and the permittivity is the same in the near-electrode layer and in the sample bulk. Then

$$W = 2d\frac{\varepsilon_{\infty 1}}{\varepsilon_{s1}}. \tag{4}$$

The W values for various samples are presented also in Table 1. Those are seen to be as small as several tenths of μm. It follows from the data obtained that, unlike τ_2, W is less dependent on the introduced impurity type.

It is shown [6] that in nematic LC, W is equal to the Debye screening length. To check if this condition is fulfilled for FELC, the ion concentrations were determined in experiment. To that end, the charge carrier mobility, μ, was measured using the technique proposed in [15]. The transition current maximum necessary to determine the charge transfer time between the electrodes, however, was observed neither in pure nor doped FELC. Thus, we can suppose only that W is equal to the Debye screening length in FELC, too. This is confirmed in part by the fact that the W value is higher in the FELC studied than in nematics. If the charge carrier mobility in FELC and nematics is assumed to be the same, then, taking into account the lower conductivity of FELC as compared to that of nematics, the Debye shielding length in FELC must be larger. Comparison of the W values obtained with data from [5, 6] evidences that it is the case in fact.

It can be concluded from the data presented in Table 2 that parameters characterizing the dispersion region II depend slightly on U_0, too. Note that at high U_0, there is a distinction as compared to the dispersion region I. While at $U_0 = 1$ V, τ_1 increases (as compared to values obtained at lower U_0), τ_2 decreases in this case.

All the above-mentioned specific features of the dispersion region II allow to believe that it is due to a local molecular orientation change in the near-electrode layer having the thickness equal to the Debye screening length. It is of interest to discuss why this relaxation process in smectic FELC phases is described by the Cole-Cole dispersion, that is, the relaxation time has no specific value but is characterized by a certain distribution function.

It follows from the conclusion on the mechanism of dispersion region II that the found relaxation times characterize the dynamics of molecular orientation in the near-electrode layer. Such dynamics is described basing on the momentum balance for elastic and viscous force. For nematic LC, the momentum balance equations has the form [16]

$$K_{22}\frac{d^2\Theta}{dz^2} = \gamma\frac{d\Theta}{dt}, \tag{5}$$

where K_{22} is the Frank elastic module; Θ, the deviation angle of the molecules from the director at zero electric field strength (for planar molecular orientation, this angle is in most cases the angle with the substrate plane); γ, the viscosity. When measuring the frequency dependences of ε' and ε'', the measuring signal voltages were much lower than the threshold value for Fredericks effect. Therefore, change in Θ must be insignificant. In this case, the Eq.(5) has an analytical solution consisting of a series of harmonics with time constants

$$\tau_n = \frac{\gamma W^2}{\pi^2 K_{22}(2n+1)^2}, \tag{6}$$

where n is the harmonic order. At small Θ changes, the above relationships can be used also for N^+ phase. That is why for that phase, a relaxation process with one single relaxation time is observed.

In smectic phases, the momentum balance equation characterizes as a rule the dynamics of the spontaneous polarization vector [12]:

$$\gamma_\varphi \sin^2\Theta\frac{d\varphi}{dt} = K_\varphi \sin^2\Theta\frac{d^2\varphi}{dz^2} - P_S E\sin\varphi, \tag{7}$$

where γ_φ is the rotation viscosity; φ, azimuth angle of molecule rotation about the helicoid axis; E, the electric field strength. The relationship (7) describes the Goldstone mode dynamics. But we have shown that the bulk polarization processes are related mainly to the soft mode. If the molecular orientation dynamics would be defined by the Θ angle only also in the near-electrode layer, then the Debye dispersion should be observed in smectic phases, too. The certain distribution function of relaxation time (Cole-Cole dispersion) present in the dispersion region II allows to suppose that the predominating molecule deviation along the Θ angle is accompanied by a slight rotation about the helicoid axis. Therefore, when considering the molecular orientation dynamics in the smectic near-electrode layer, not only Eq.(5) but in part also the Eq.(7) is to be taken into account. It is just the electrode surface inhomogeneity that may be among reasons for the mode mixing; its effect is described in detail in [17]. The possibility to describe the complex process of molecular orientation change in the near-electrode layer basing on a single relationship will be discussed in a further work.

It follows from Fig. 2 that the dispersion regions I and II are rather close to one another on the frequency scale being essentially overlapped for the FELC+0.4 % TI. Therefore, it is of interest to consider relationships between the bulk and near-electrode relaxation processes. This question can be answered in part by analyzing the maximum ε'' value for the dispersion region I. The experimental data obtained evidence that ε''_{max} depends not only on molecular orientation but also on the impurity presence. The dopants introduced did not effect the phase transition temperatures, as mentioned above. Thus, the bulk FELC properties must remain unchanged in the presence of such impurities. Therefore, the dispersion region I is to be supposed to correspond not to bulk processes in the strict sense but to "extended" near-electrode ones. This supposition combined with the Eq.(4) results in the conclusion that the higher is ε''_{max} value, the narrower is the region where the molecular orientation changes. As is seen in Fig. 2, the highest $\varepsilon''_{max} = 16.4$ was obtained for the FELC+1.1 % D_1. It follows from Eq.(4) that the layer where the molecular orientation takes place predominantly is 4.5 μm. This is one order larger than the layer where relaxation process causing the dispersion region II takes place.

Thus, two dispersion regions, I and II, have been revealed in dielectric spectra of FELC consisting of a mixture of 4-*p*-hexyloxyphenyl-4-*p*-octyloxybenzoate and 4-*p*-hexyloxyphenyl-4-*p*-decyloxybenzoate (62.3 and 31.2 % by mass, respectively) containing a polar chiral admixture LUCH-15 (6.5 % by mass). The higher-frequency dispersion region I has been shown to be due to the soft mode in SmA phase and to the Goldstone one in SmC*. The dispersion parameters in this region are essentially independent of the dopant presence and molecular orientation.

The dispersion region II is due to local change of molecular orientation in the near-electrode layer of a thickness equal to the Debye screening length. The reasons for dependence of parameters characterizing this dispersion region on the dopant presence have been elucidated. This relaxation process in isotropic and chiral nematic phases is described by the Debye equation while in smectic ones, by the Cole-Cole equation. The "blurred" relaxation time in smectic phases may be caused by complex character of the orientation change involving a rotation of molecules about the helicoid axis in addition to their deviation in the plane of that axis. The dependence of maximum ε'' value (in the dispersion region I) on the dopant concentration is supposed to be due to a partial localization of the process in the near-electrode layer. The estimated thickness of that layer has been shown to excess by one order the Debye screening length.

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References

1. A.V.Koval'chuk, *Functional Materials*, **5**, 426(1998).
2. A.V.Koval'chuk, *Functional Materials*, **8**, 690(2001).
3. A.Sawada, H.Sato, A.Manabe et al., *Jpn.J. Appl.Phys.*, **39**, 3496(2000).
4. M.Y.Jin, J.-J.Kim, *J.Phys.:Condens.Matter*, **13**, 4435(2001)
5. A.V.Koval'chuk, *Technical Physics Letters*, **26**, 849 (2000).
6. A.V.Koval'chuk, *Technical Physics Letters*, **27**, 202(2001).
7. L.M.Blinov, L.A.Beresnev, *Usp.Fiz.Nauk*, **143**, 392 (1984).
8. G.Chilaja, V.G.Chigrinov, *Usp.Fiz.Nauk*, **163**, 1(1993).
9. A.Levstik, T.Carlsson, C.Filipic et al., *Phys. Rev.A*, **35**, 3527 (1987).
10. R.J.Cava, J.S.Patel, K.R.Collen et al., *Phys. Rev.A*, **35**, 4378(1987).
11. H.Xu, J.K.Vij, A.Rappaport et al., *Phys.Rev. Lett.*, **79**, 249 (1997).
12. A.Levstik, Z.Kutnjak, C.Filipic et al., *Phys. Rev.A*, **42**, 2204 (1990).
13. F.J.Twarowski, A.C.Albrecht, *J.Chem.Phys.*, **70**, 2255(1979).
14. A.V.Koval'chuk, M.N.Pivnenko, *Ukr.Fiz.Zh.*, **47**, 154 (2002).
15. N.I.Gritzenko, N.V.Moshel, *Ukr.Fiz.Zh.*, **25**, 1830(1980).
16. L.V.Blinov, Electro-Optical and Magneto-Optical Properties of Liquid Crystals, Wilej, New York (1983).
17. L.V.Mirantsev, *Phys.Rev.E*, **59**, 5549(1999).

Нізькочастотна діелектрична спектроскопія сегнетоелектричних рідких кристалів: приелектродні та об'ємні процеси

О.В.Ковальчук, О.Ф.Шевчук, Д.А.Найко, М.М.Півненко

В интервалі частот 10^{-3}–10^{5} Гц та температур 310–370 К досліджені частотні залежності компонент комплексної діелектричної проникності сегнетоелектричного рідкого кристалу (СРК) як в чистому виді, так і з наявністю сильно и слабо дисоціюючих домішок. Знайдено дві області дисперсиї. Показано, що більш високочастотна область дисперсії I спостерігається тільки в смектичних фазах. Час її релаксації складає в середньому 0,7 мс та слабо залежить від наявності домішок. Область дисперсії II спостерігається у всіх фазах планарно орієнтованого СРК. На її параметри суттєво впливає наявність домішок. Показано, что дана область дисперсії зумовлена локальною зміною орієнтації молекул в приелектродній області, товщина якої рівна дебаєвскій довжині екранування. Зроблено припущення, що причиною "розмитого" часу релаксації в смектичних фазах може бути складний процес зміни орієнтації молекул, який включає як зміну смектичного кута нахилу, так і частове обертання навколо осі гелікоїда.