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PHOTON CORRELATION SPECTROSCOPY FOR INVESTIGATION OF VISCOUS-ELASTIC PROPERTIES OF SHOCK-FREE FERROELECTRIC LIQUID CRYSTAL

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Photon correlation spectroscopy was applied for the first time to study viscous-elastic properties of ferroelectric liquid crystal showing relatively high fluidity in smectic C phase (shock-free FLC). The spectral analysis of correlation functions made it possible to calculate viscous-elastic ratios defining dynamics of Goldstone mode of director's fluctuations. The obtained results were discussed taking into account the data on elastic and viscous parameters derived from independent experiments.*

Key words: ferroelectric liquid crystal, photon correlation spectroscopy, viscous-elastic properties.

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ФОТОННАЯ КОРРЕЛЯЦИОННАЯ СПЕКТРОСКОПИЯ ДЛЯ ИССЛЕДОВАНИЙ ВЯЗКО-УПРУГИХ СВОЙСТВ СТРЕССОУСТОЙЧИВОГО ФЕРРОЭЛЕКТРИЧЕСКОГО ЖИДКОГО КРИСТАЛЛА

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Техника динамической корреляционной спектроскопии впервые применена для исследования вязко-упругих свойств сегнетоэлектрического жидкого кристалла (СЖК) с относительно высокой текучестью в смектической С фазе (стрессоустойчивый СЖК). Спектральный анализ корреляционных функций позволил рассчитать вязко-упругие отношения, определяющие динамику Голдстоуновской моды флуктуаций директора. Полученные результаты обсуждаются с учетом данных по упругим и вязкостным параметрам, полученным из независимых экспериментов.*

Ключевые слова: ферроэлектрические жидкие кристаллы, фотонная корреляционная спектроскопия, вязко-упругие свойства.

Introduction

Among number of experimental methods used for measurement of elastic and viscous properties of liquid crystals (LC), the photon correlation spectroscopy showed essential advantages as a universal field free tool for studying liquid crystal systems of different types, such as plane layers of liquid crystals [1, 2], porous glasses [3] and polymer films filled with LC [4, 5]. This technique is based on study of frequency spectrum of dynamic light scattering (DLS) induced by thermal fluctuations of director which is described in terms of the autocorrelation function of the scattered intensity [6]. This function is computed via electronic manipulation with the intensity of scattered light registered at different times by the photocathode of a photomultiplier. For plane layers of nematic liquid crystals (NLC) it is possible to establish each of Frank's modules and combinations of viscous coefficients by measuring the intensity of scattered light and decay rate of the correlation function at different scattering geometries. Moreover, it also provides determination of the polar and azimuth anchoring strengths, which characterize the interaction of nematic LC with a solid surface [7, 8]. Application of this technique to porous glasses [3] and porous polymer films [5] made it possible to extract unique information on viscous properties of NLC at strong confinement.

It is of importance, that not only nematic phase, but also some smectic phases can be studied by the photon correlation spectroscopy. In particular, in smectic C phase (SmC) with long molecular axes inclined on the angle θ respectively to the normal of the smectic planes, a quasi nematic motion of a director along the cone surface, restricted by the condition $\theta = \text{const}$, is possible. It differs from the case of smectic A phase (SmA), where the director's motion is strongly suppressed due to connection of such motion with the corresponding deformation of the layer structure. So, one can wait the essentially different character of thermal fluctuations of a director and light scattering characteristics for two smectic phases mentioned above.

The chiral smectic C phase (SmC*), which differs from SmC phase only by the helical orientational structure, is of a special interest as it shows ferroelectric properties, important for practical applications. Such ferroelectric liquid crystals (FLC) were studied by many experimental methods, including the photon correlation spectroscopy [9–11]. In particular, the combinations of viscous-elastic parameters, responsible for

dynamics of the director fluctuations were extracted by analysis of time correlation function of the scattered light for FLC with different values of helix pitch P [10, 11]. The essential difference in the values of viscous-elastic parameters of different FLC was established experimentally. At the same time, the question about the reason of such difference is open up to now.

In this paper, we present first results on investigation of the shock-free liquid crystal FLC-595 by the photon correlation spectroscopy. Such materials are very promising for practical applications as they restore the initial optical properties after shock type mechanical stresses. The obtained viscous-elastic parameters are compared with the results of independent experiments and analyzed taking into account our previously published results on elastic and viscous properties of FLC-595 [12].

Experimental

The photon correlation spectroscopy applied for investigation of viscous-elastic parameters of FLC is based on the analysis of the angular dependences of the relaxation time τ_G of the so-called Goldstone mode of director fluctuations in SmC* phase. Values τ_G can be extracted from spectra of the autocorrelation function $G_{11}(\tau)$ of light scattering which is expressed as [13].

$$G_{11}(\tau) = \langle I_1(t) \cdot I_1(t + \tau) \rangle, \quad (1)$$

where τ is delay time; angle brackets denote time averaging. This function describes correlation between the scattered light intensity $I_1(t)$ at a given time and the scattered light intensity $I_1(t + \tau)$ at time $t + \tau$.

In the normalized to unit form, the specified autocorrelation function for the given diffusive mode with decay rate Γ is expressed as:

$$g_2(\tau) = 1 + e^{-2\Gamma\tau}, \quad (2)$$

where Γ is half-width of spectral line of scattered light, equal to the inverse relaxation time $1/\tau$ (in our case τ equals to τ_G).

Previously, the angular dependence of the inverse relaxation time $\tau^{-1}(\theta)$ of the autocorrelation function of light scattering $g_1(\tau)$ in the frequency range of 1..10 kHz was used to determine viscoelastic characteristics of ferroelectric liquid crystals [11] in accordance with the expression:

$$\frac{1}{\tau_G} = \frac{K_2}{\gamma} (q_z - q_0)^2 + \frac{K_+}{\gamma} q_x^2, \quad (3)$$

where q_0 is the wave vector of the helix, given by the relation:

$$q_0 = 2\pi / P, \quad (4)$$

where P is the helix pitch with the axis directed along Z axis; q_x and q_z are projections of the scattering wave vector on X and Z axes, shown in Fig. 1, γ is the viscosity coefficient; the module $K_+ = (K_1 + K_3)/2$; K_1 , K_2 and K_3 are elastic constants corresponding to "splay", "twist" and "bend" deformations, correspondingly.

Values q_x and q_z at a given scattering angle θ_s can be represented as [11]:

$$q_z = |q| \sin(\theta_s / 2) \quad (5)$$

$$q_x = |q| \cos(\theta_s / 2) \quad (6)$$

$$|q| = \frac{4\pi}{\lambda} \sin(\theta_s / 2), \quad (7)$$

where λ is wavelength of the incident radiation.

In our experiments, we used the shock-free FLC-595 developed at mixing of nematic host and chiral non-mesogenic guest, which forms ferroelectric SmC* phase at $T_c \approx 40$ °C on cooling from isotropic phase through smectic A phase. Some useful information about this mixture and its parameters, including viscous-elastic characteristics, obtained by different experimental methods, was presented in our previous paper [12].

In the comparison with other FLC independently studied by the same method, this mixture is characterized by the essentially smaller values of a helix pitch, lying in submicron range, and by higher fluidity. The liquid crystal flat cell with the gap of 60 μm was filled by LC in the isotropic phase. The inner surfaces of glass substrates were covered with the layer of chromolan to provide homeotropic surface orientation of director. Quality control of orientation was ensured by observation of sample in crossed polarizers.

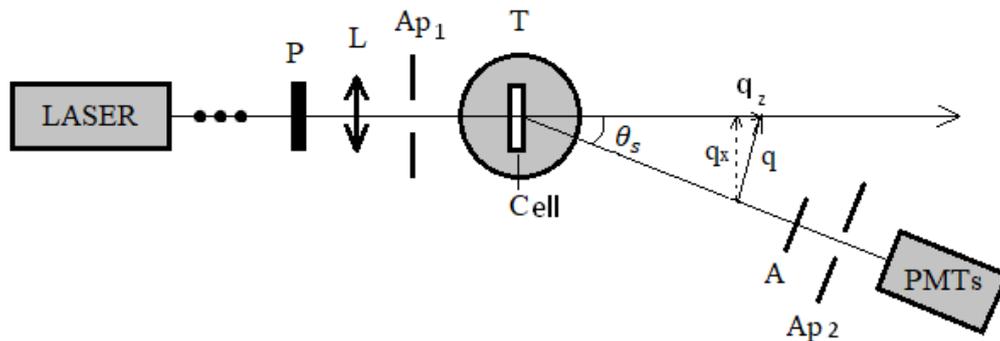


Fig. 1. The geometry of the experiment according to [11] and the main elements of our experimental setup:

LASER – He-Ne laser with vertical polarization of the beam, P – polarizer, L – lens, Ap₁ – Cell–cell, T – thermostat, A – analyzer, Ap₁ and Ap₂ – diaphragms, PMTs – a photomultiplier equipped with a photon counting unit and a correlator.

All measurements in our experiments were performed with usage of the photon correlation spectrometer "Photocor complex" (Russia)

In our experiments, performed in accordance with a geometry shown in Fig. 1, the incident laser radiation with a vertical, relative to the scattering plane, polarization propagated along the normal to the plane of the cell. The output radiation scattered at the given θ_s passed through the analyzer (A), crossed relatively to the polarizer, was registered by the PMTs photomultiplier with further primary processing by the photon counter (not shown in the figure) to provide a number of photo counts units (typically from 10^5 to $2 \cdot 10^6$ photo counts per second (cps)).

The value of counts proportional the intensity of the scattered light I made it possible to determine the correlation function of the dynamic light scattering via a special device – the 288 channel correlator with a time step equaled to 10 ns and the total time range from 100 ns to 10^3 s.

DynaLS program was used to process the autocorrelation functions of light scattering. The results of application of this program is shown in Fig. 2.

In this study, the main attention was paid to the peak at about 0.003 MHz, which reflects the Goldstone mode of the director's oscillations.

It should be noted that the transition from SmA to SmC* phases of the FLC-595 is also registered by a

sharp change in the scattered light intensity I , observed at $T_c \approx 38^\circ\text{C}$ (see Fig. 3).

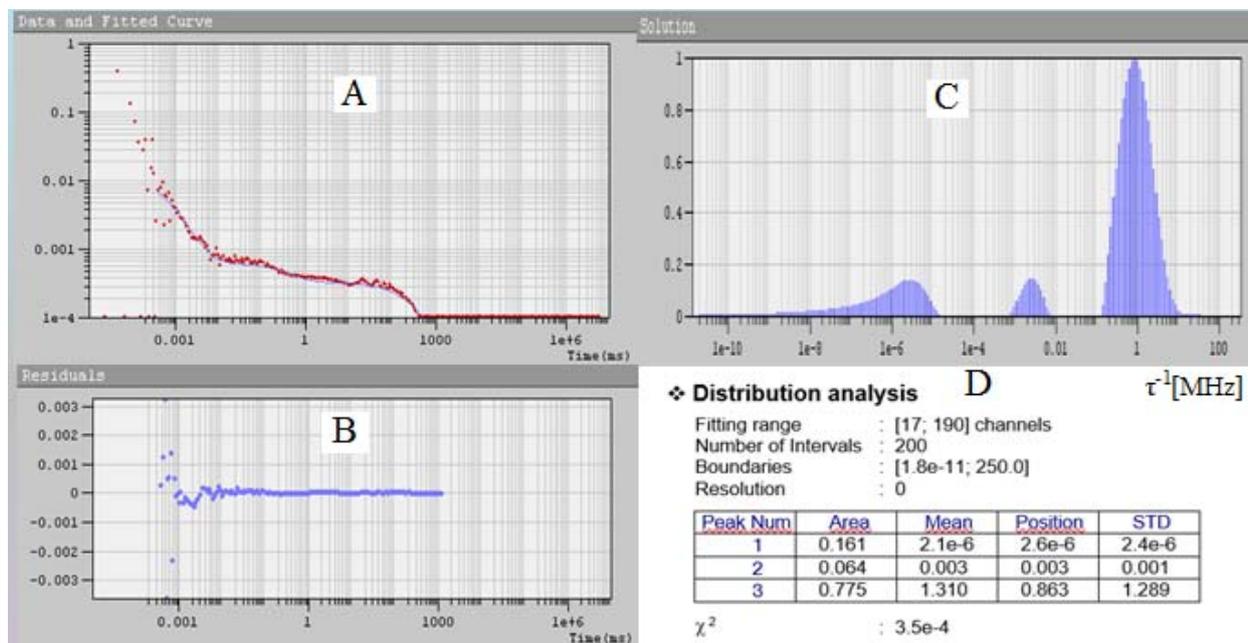


Fig. 2. A typical view of experimental data after initial processing by DynaLS program:

A – autocorrelation function $g_1(\tau)$ for dynamic light scattering in the sample FLC-595; B – deviations of experimental data from the theoretical model; C – spectral distribution of inverse relaxation times of the autocorrelation function; D – numerical values of inverse relaxation times of the autocorrelation function. The data were obtained at a scattering angle $\theta = 7.5^\circ$, at $T - T_c = -2^\circ\text{C}$

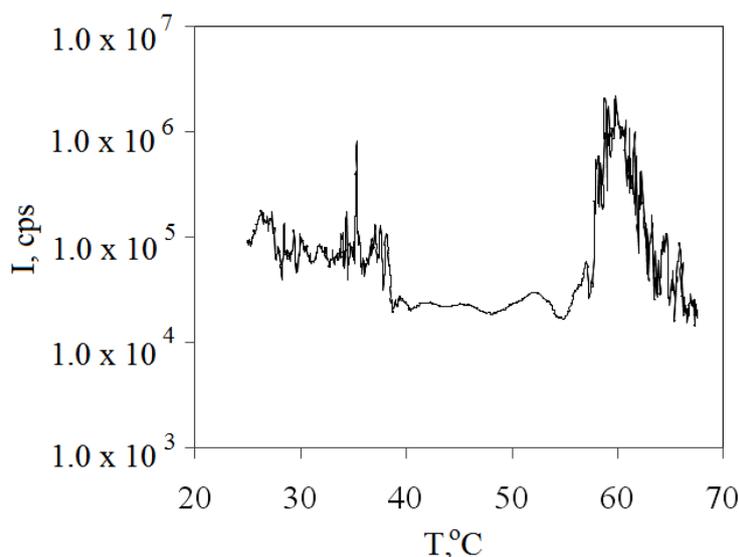


Fig. 3. Temperature dependence of the light scattering intensity I in the sample FLC-595 at heating mode with the speed of 0.6 K/h; the incidence angle of the beam on the cell is 13.5° , the scattering angle is 141.5° , laser polarization (P) is vertical (0°), position of analyzer is horizontal (90°)

Experimentally determined dependences of the inverse relaxation time τ_G^{-1} on the scattering angle at different temperatures in SmC* phase of FLC-595 are presented in Fig. 4.

The values of the viscous – elastic ratios, determined via approximation of experimental data by the theoretical dependence, are shown in Table 1.

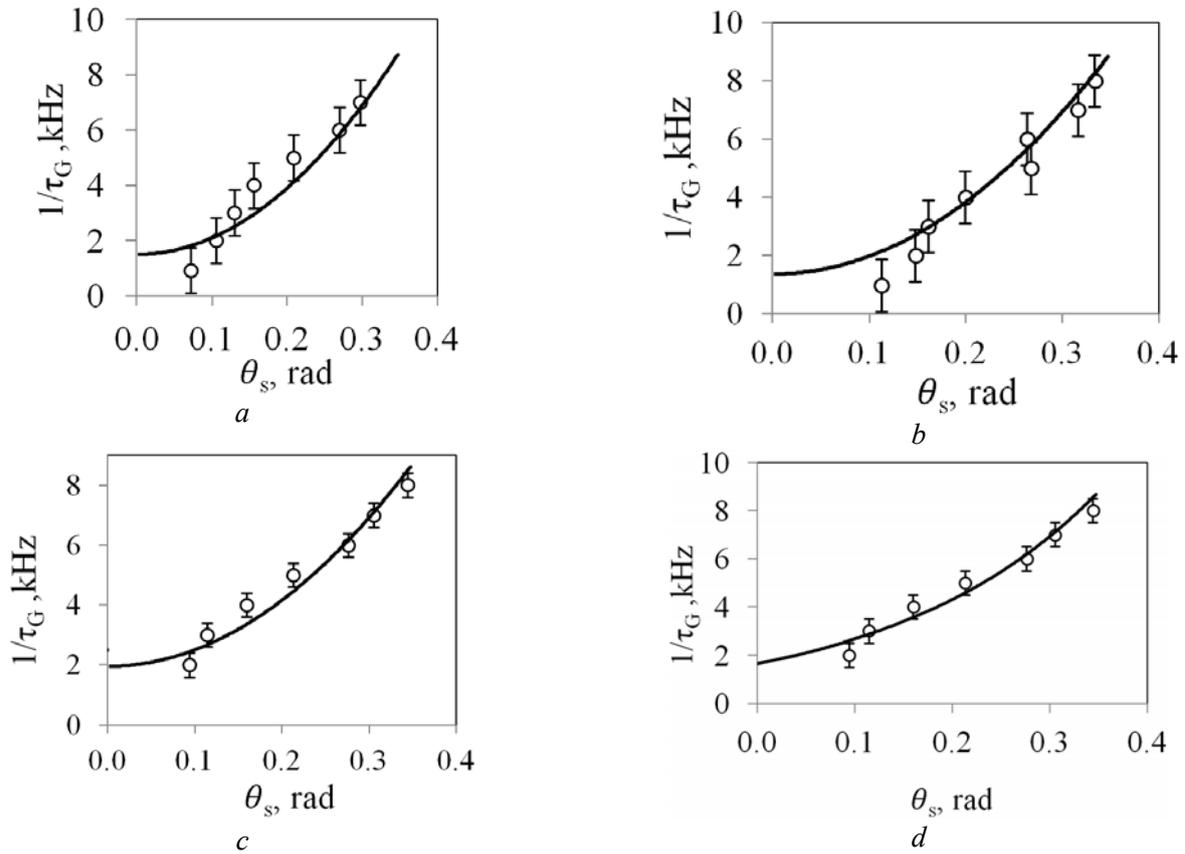


Fig. 4. Dependence of τ_G^{-1} on θ_s for FLC-595 at different temperatures: *a* – 28 °C, *b* – 29 °C, *c* – 30 °C, *d* – 31 °C. Circles show experimental data, the line is theoretical model

Table 1. Pitch P [12] and viscoelastic coefficients of FLC 595

| T_s , °C | P , μm | q_0 , μm^{-1} | K_2/γ , $\text{m}^2 \text{s}^{-1}$ | K_+/γ , $\text{m}^2 \text{s}^{-1}$ | γ , Pa*s |
|------------|---------------------|----------------------------|---|---|-----------------|
| 33 | 0.621 | 10.13 | 7.5×10^{-12} | 6.8×10^{-10} | 0.84 |
| 32 | 0.603 | 10.43 | 1.1×10^{-11} | 7.7×10^{-10} | 0.57 |
| 31 | 0.585 | 10.73 | 6.8×10^{-12} | 8.0×10^{-10} | 0.93 |
| 30 | 0.569 | 11.05 | 9.9×10^{-12} | 7.2×10^{-10} | 0.64 |
| 29 | 0.553 | 11.37 | 6.0×10^{-12} | 6.9×10^{-10} | 1.05 |
| 28 | 0.520 | 12.08 | 1.7×10^{-11} | 7.8×10^{-11} | 0.37 |

It is interesting that our data on the K_+/γ ratio are close to the investigation result of another FLC CE8 ($K_+/\gamma \approx 4 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ [10]), with the comparable pitch value ($P_0 \approx 1.2 \mu\text{m}$). While the data for FLC material ZL5014-100 ($K_+/\gamma \approx 5 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$) [11] with larger helix pitch (about $4 \mu\text{m}$) are essentially differ from our

results. At the same time, in our case the values of the ratio K_2/γ are about 2 orders of magnitude less than the corresponding values, obtained for the other FLCs mentioned above ($K_2/\gamma \approx 2 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for CE8 and $K_2/\gamma \approx 6 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for ZL5014-100). At qualitative level, this is consistent with the conclusion made in the previous

work [12] on the significantly lower values of the effective elastic module $K_\phi \approx K_2$ for the shock-free FLC-595 in comparison with the data, obtained for other FLC, which do not show sufficiently high fluidity. Using the effective elasticity modulus value $K_\phi \approx 6.8 \cdot 10^{-12}$ N [12], it is possible to estimate the viscosity γ , included in the initial theoretical expressions from the obtained data. The result of this estimation is shown in Table 1. It should be noted that the viscosity values are of the same order of magnitude as the normalized values of the rotational viscosity of the C director and the shear viscosity obtained by an independent rheological methods [12]. The obtained results confirm the effectiveness of the photon correlation spectroscopy for a study of viscoelastic properties of ferroelectric smectics C.

Conclusion

The viscous-elastic properties of the ferroelectric liquid crystal FLC-595 with submicron helix pitch and high fluidity were determined by dynamic light scattering (DLS) connected with Goldstone mode of thermal director's fluctuations. The inverse relaxation times $\tau^{-1}(\theta)$ of the autocorrelation function of light scattering $g_1(\tau)$ in the frequency range of 1..10 kHz at different scattering angles were used to calculate two ratios: K_2/γ and K_+/γ ($K_+ = (K_1 + K_3)/2$) of Frank's moduli K_i to the effective rotational viscosity γ at different temperatures. The obtained results were compared with the data of independent DLS measurements of some traditional FLC, which did not show shock-free behavior. It was found that the values of K_+/γ for FLC-595 are of the same order of magnitude as those for FLC CE8 with a comparable helix pitch. At the same time, the values of the ratio K_2/γ were surprisingly lower (approximately by two orders of magnitude), than those found for FLC CE8 and ZL5014-100. The obtained results corresponds to the previously reported ones [12] about relatively small values of the effective twist module $K_\phi \approx K_2$ for the shock-free FLC-595. The estimated values of the effective rotational viscosity γ extracted from DLS measurements are also of the same values of magnitude as those for the normalized rotational viscosity and shear viscosity [12].

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