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RELAXATION PROCESSES IN ISOTROPIC PHASE OF CHOLESTERYL MYRISTATE

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Relaxation Processes in Isotropic Phase of Cholesteryl Myristate

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The paper reports on study of acoustic parameters in isotropic phase of Cholesteryl Myristate within a frequency range from 2 MHz to 7 HHz. It was observed, that in the range of hypersonic frequencies on a background of a relaxation process with a significant dispersion of sound velocity and characteristic frequency dependence of hypersonic absorption another relaxation process appeared. Hence, it is may be assumed that at least three relaxation processes occur in the isotropic phase of CM within the investigated frequency range. First relaxation process (from 1 HHz to 7 HHz), and third relaxation process (from 2 MHz to 22 MHz) are analogous to those observed for the isotropic phase of the nematic MBBA. The second relaxation process observed in the range of hypersonic frequencies is characteristic only for the isotropic phase of CM and it is not observed for nematics. The nature of this relaxation process is discussed.

Keywords: acoustic relaxation; Cholesteryl Myristate; hypersound; isotropic phase; light scattering; ultrasound

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INTRODUCTION

A relaxation time is usually used as a fundamental information parameter when a dynamics of phase transitions is investigated. Although a dynamic behavior of cholesterics on molecular level is still not well known, it is possible to indicate some basic classes of relaxation processes in isotropic phase.

First class contains the relaxation processes connected with a relaxation of order parameter fluctuations. Isotropic phase has no long-range order in a direction of molecular axes, and order parameter tensor is equal to zero. However, for rather small time-space scales a local order exists for some distance ζ called a correlation length. In Landau - de Gennes approach ζ is determined as follows:

$$\zeta(T) \approx l\left[T^* / (T - T^*)\right]^{\frac{1}{2}}$$

Here l is molecular length, T - temperature, and T^* - critical temperature. It has good agreement with experimental results for intensity of scattered light in isotropic phase of nematics [1]. However, there is a deviation from linear dependence of inverse integral intensity very near the phase transition connected with fluctuation contributions [2,3]. Much more significant deviation from linear dependence of inverse integral intensity takes place in isotropic phase of Cholesteryl Myristate (CM) [4]. It is connected with "structure" fluctuations, which are, probably, characteristic for isotropic phase of CM, as it will be shown later. Relaxation time for order parameter fluctuations of nematics lies in limits of 10^{-8} - 10^{-6} sec. At the same time for CM it is of 10^{-7} - 10^{-5} sec. [4].

Second class of relaxation processes is connected with a rotation of molecules along their major axes and translational self-diffusion. Relaxation time of such processes is slightly dependent on temperature (by comparison with the relaxation processes of first class). Estimated values of relaxation times for such processes are 10^{-9} - 10^{-12} sec.

Another class of relaxation processes in isotropic phase of liquid crystals is intra-molecular relaxation connected with a motion of molecular end-groups. Such relaxation processes also have weak temperature dependence of relaxation time and its value can be equal to

10^{-8} - 10^{-12} sec. For example, the value of intra-molecular relaxation time for nematic p-methoxybenzylidene-butylaniline (MBBA) is equal to 10^{-9} sec.

Thus, to provide a complex investigation of the relaxation processes in isotropic phase of cholesterics it is necessary to apply new methodologies in order to obtain an information about the relaxation times having values from 10^{-6} sec. to 10^{-12} sec. The present paper reports on study of acoustic parameters in isotropic phase of CM within a wide frequency range (2 MHz - 7 HHz) and temperature range from 100 ^{0}C to 84 ^{0}C in order to obtain the information about the relaxation processes and their parameters. In the frequency range from 2 MHz to 22 MHz a pulse method based on the diffraction of light due to ultrasound waves was used. In the frequency range from 1.1 HHz to 7 HHz we used the method of Mandelshtam-Brillouin light scattering spectroscopy. For both methods, one and the same sample of CM was used.

To describe relaxation processes connected with order parameters fluctuations in liquid crystals, a correlation function characterizing the fluctuations of order parameter tensor was introduced [6,15]:

$$G(q) \approx \frac{Vk_BT}{2(A+Lq^2)}$$

Here V is volume, k_B - Boltzman constant, q - wave vector, A and L - coefficients of Landau free energy expansion.

$$A(T) = a(T-T^*),$$

where a is a coefficient of proportionality.

It is assumed that the connection of $G(q) < 0$ with sound wave is determined by changes of $A(T)$ with temperature oscillations conditioned by an influence of sound wave. Near the point of phase transition, where the fluctuations are characterized by strong spatial correlation, the response of $G(q)$ to the oscillation of local temperature cannot be instantaneous. In addition, that leads to increase in absorption of sound and dispersion of sound velocity. Theory gives the following expression for $(\alpha\lambda)_{exc.}$ (λ is sound wavelength; $\alpha_{exc.}$ is exceed of sound absorption connected with order parameters fluctuations), and sound velocity as a function of temperature and frequency:

$$\alpha_{exc}\lambda = \pi(\gamma_0 - 1)(\Delta C_p / C_p^0)F_2(x) \quad (1)$$

$$(V - V_0)/V_0 = -\frac{1}{2}(\gamma_0 - 1)(\Delta C_p / C_p^0)F_1(x) \quad (2)$$

Here $\gamma_0 = C_p^0 / C_v^0$; V_0 - adiabatic velocity of sound in the absence of order parameters fluctuations; C_p^0 and C_v^0 are, respectively, heat capacity at constant pressure and at constant volume in the absence of the fluctuations; ΔC_p - exceed of heat capacity connected with the fluctuations;

$$F_1(x) = \sqrt{2x}\left[x + (1+x^2)^{\frac{1}{2}}\right]^{-\frac{1}{2}} \quad (3)$$

$$F_2(x) = \sqrt{2x}\left\{\left[x + (1+x^2)^{\frac{1}{2}}\right]^{\frac{1}{2}} - \sqrt{2x}\right\} \quad (4)$$

Here $x = f_r / f$ is characteristic relaxation frequency, $f_r = A(T)/2\pi\xi$ - relaxation frequency in a long-wave region ($q=0$), ξ- some "effective" kinetic coefficient having a dimension of that for viscosity, f - frequency of sound.

For practical analysis of obtained results, we use the expression for exceed of absorption and dispersion determined as follows:

$$(\alpha\lambda)_{exc} = \pi B(T) F_2(f_r / f) \quad (5)$$

$$\frac{V_\infty^2 - V^2}{V_\infty^2} = [B(T)/2]F_1((f_r / f) \quad (6)$$

Here V_∞ is the velocity of sound at rather high frequencies, and $B(T) \approx \frac{\Delta C_p}{C_p^0}$ as it was shown in [7].

MEASUREMENTS

To determine the values of ultrasound velocity and absorption, the method based on the diffraction of light due to ultrasound waves was used. The experimental set-up was modified to operate in pulse regime that is the necessary condition to provide measurements near phase transition, where the susceptibility of liquid crystals is very large. The results of measurements of sound velocity and absorption at the frequencies of 2 MHz, 3 MHz, 9 MHz, 16 MHz and 22 MHz were presented in our previous paper [8].

The velocity of ultrasound propagation was measured from the value of diffraction angle, and the intensity of diffracted light, depending on a distance from emitting transducer, contains the information about ultrasound absorption. The accuracy of the measurements of sound velocity and absorption was, consequently, 0,5% and 10%.

Hypersonic velocity and absorption over a frequency range 1-7 HHz was determined by Mandelshtam - Brillouin components' shift and width [9]. The spectra were registered for light scattering angels $19.6^0 \pm 0.2^0$, $90^0 \pm 0.2^0$, and $167^0 \pm 0.2^0$ using spectral set-up with double-passed Fabry-Perot interferometer (for more detailed description see [10]). The contrast of interference pattern was $5 \cdot 10^4$, and the sharpness was 35. The regime of two passes allowed to investigate Mandelshtam-Brillouin light scattering spectra very near the phase transition. The accuracy of determination of hypersonic velocity and absorption was dependent on scattering angle: from 1% to 0.5% for the velocity measurements, and from 20% to 10% for measurements of absorption coefficient. The errors of measurements decrease with increasing scattering angle.

The CM sample was purified by repeated recrystallization in n-hexane and was then pressed through a filter with pores of diameter 0.2 μm under vacuum to the cell to remove dust. The cell with the sample was thermostatted to ± 0.01 ^{0}C. The clarification temperature of the sample upon heating the cholesteric phase was 83.2 ± 0.1 ^{0}C. The

temperature of fog phase upon cooling isotropic phase was 83.6 ± 0.1 ^{0}C.

RESULTS AND DISCUSSION

The results of temperature dependence of hypersonic velocity for three scattering angles are presented in Figure 1. Here are also presented the results of measurements of ultrasound velocity over the frequency range 2-22 MHz.

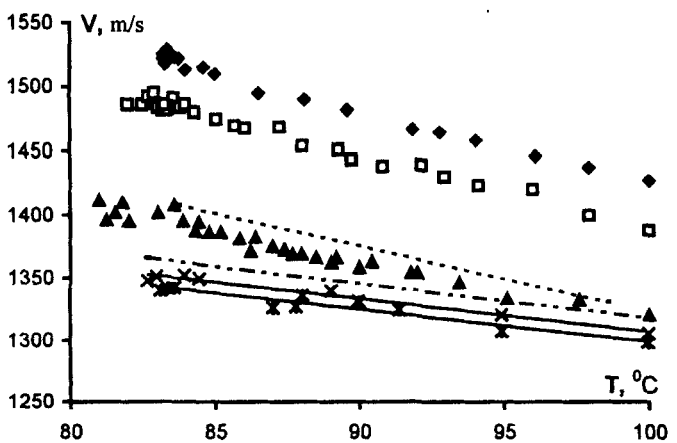

FIGURE 1

Temperature dependence of sound velocity in isotropic phase of Cholesteryl Myristate.
(♦-6.5 HHz; □-4.5 HHz; ▲-1.1 HHz; ×-22 MHz; *-2 MHz; dotted line – V_0; double-dotted line - V_∞; solid lines – results of calculations using Eq.(6))

Figure 2 presents the temperature dependence of absorption coefficient multiplied by wavelength of sound for three scattering angles (frequencies).

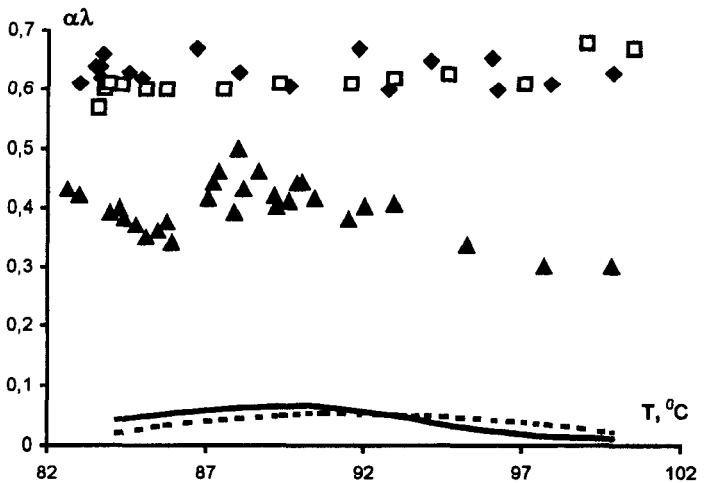

FIGURE 2

Temperature dependence of absorption coefficient multiplied by wavelength for three scattering angels (frequencies).
(▲ 6.5 HHz; □-4.5 HHz; ♦-1.1 HHz; Results of calculation are presented by solid line for 1.1 HHz, and dotted line for 4.5 HHz.)

Significant dispersion of sound velocity observed in isotropic phase of the liquid crystal (Figure 1) and frequency dependence of sound absorption indicate the existence of relaxation process in hypersonic frequency range. Moreover, some specific behavior of the hypersonic velocity depending on temperature for scattering angle of $19{,}6^0$ (frequency 1.04 - 1.12 HHz) should be pointed out. If the values

of temperature coefficient of the velocity $\frac{\partial V}{\partial t}$ at frequencies of 6.5-7 HHz (scattering angle 167^0) and 4.5 - 4.9 HHz (scattering angle 90^0) are identical and equal to 3.0 $m \cdot sec^{-1} \cdot {}^0C$ (for ultrasound 22MHz $\frac{\partial V}{\partial t} = 1.5$ $m \cdot sec^{-1} \cdot {}^0C$) then at the frequencies of 1.04 - 1.12 HHz (scattering angle 19.6^0)the dependence of sound velocity on temperature cannot be described by straight line with constant $\frac{\partial V}{\partial t}$.

It can be assumed that in CM on the background of relaxation process characterized by significant dispersion of sound velocity and typical frequency dependence of hypersonic absorption, analogous to that observed in isotropic phase of nematic MBBA [11], there is another (second one) relaxation process.

By analogy with our results obtained for nematics [11] we determined the parameters of first relaxation process with significant dispersion of hypersonic velocity using the equation for relaxation process with single relaxation time [12]:

$$\left(\frac{V_f}{V_0}\right)^2 = 1 + \varepsilon \frac{\left(f/f_r\right)^2}{1 + \left(f/f_r\right)^2}$$

Here ε is relaxation force, V_0 is sound velocity at low values of frequency (in our case V_0 is the value of sound velocity obtained for ultrasound at 22 MHz).

Since we carried out measurements in hypersonic range, for three frequencies, it is possible to construct a system of equations in order to determine ε and f_r parameters. Moreover, from experimental measurements of α/f^2 for three frequencies we were able to calculate f_r and the coefficients A and C as follows [12]:

$$\left(\alpha/f^2\right) = C + \frac{A}{1 + \left(f/f_r\right)^2}$$

As a result of calculations using dispersion of hypersonic velocity and absorption in CM, the values of relaxation frequency presented in Table 1, were obtained.

TABLE 1.

Temperature (°C)	Relaxation frequency f_r (HHz) (by dispersion of sound velocity)	Relaxation frequency f_r (HHz) (by sound absorption)
100	2.6	2.8
87	2.55	2.7
84	2.5	2.6

The basic criterion of correctness for applicability of calculations using the equation with single relaxation time is the equality of the values of f_r obtained from hypersonic dispersion and hypersonic absorption.

As it can be seen from Table 1, relaxation frequency weakly depends on temperature. It may be assumed, that present single relaxation process can be connected either with rotation of CM molecule along major axis, or with librations of molecule along minor axis, i.e. vibration relaxation. For more concrete determination of the nature of this process, it is necessary to attract the results of other experiments, such as Rayleigh light scattering, vibrational spectroscopy, etc. Unfortunately, it cannot be done in present paper. Let's look at the graphs presented in Figure 1 and Figure 2. Temperature dependence of hypersonic velocity and absorption at the frequency of ~ 1.1 HHz indicates the existence of second relaxation process. Its parameters, in contrast to first one, depend significantly on temperature. Since the parameters of second relaxation process depend significantly on closeness to phase transition, it can be assumed that it is connected with a certain critical fluctuations, and the nature of these fluctuations will be discussed later. To analyze the parameters of second relaxation process we used the results of theory [6], and Eqs.(5) and (6) specifically.

As $V_0(t)$ we used temperature dependence of ultrasound velocity at the frequency of 22 MHz. Temperature dependence of hypersonic velocity at the frequency of ~6.5 HHz was taken for upper limit of the velocity $V_\infty(T)$ as the first approach for second relaxation process which appears at the frequency of ~1.1 HHz.

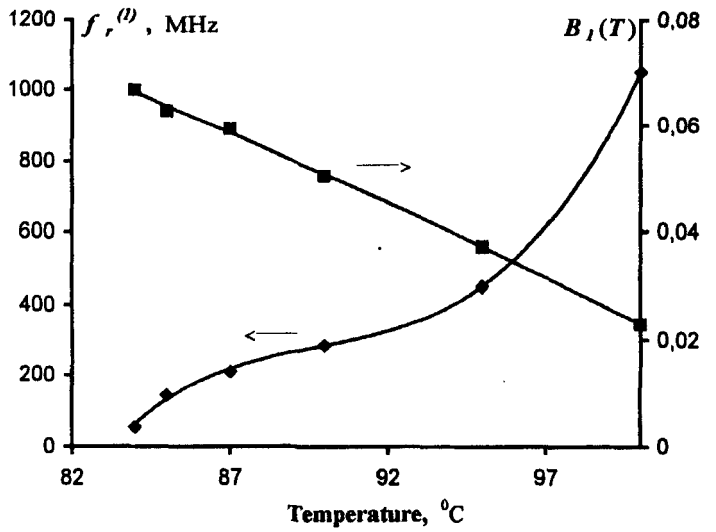

FIGURE 3

Temperature dependence of function $B_1(T)$ and relaxation frequency $f_r^{(1)}$

Since second relaxation process appears on the background of first relaxation process with significant dispersion of hypersonic velocity, we made parallel transfer of temperature dependence for $V_0(T)$ and $V_\infty(T)$ onto the graph of the temperature dependence of hypersonic velocity at ~1.1 HHz (Figure 1). From $V_0(T)$ and $V_\infty(T)$ one can determine the values of function $B_1(T)$ using Eq.(4).

$$\frac{V_\infty^2 - V_0^2}{V_\infty^2} = B_1(T)$$

since $F_2(f_r/f) \to 0$ when $f_r/f \to 0$, and $F_2(f_r/f) \to 1$ when $f_r/f \to \infty$.
Temperature dependence of $B_1(T)$ is presented in Figure 3.
Then from the values of hypersonic velocity at 1.1 HHz, values of function $B_1(T)$ and a shape of function $F_1(f_r/f)$ proposed in [6], we determined the values of $f_r^{(1)}$ for each temperature point. The results of calculations are presented in Figure 3.

As it can be seen from Figure 3, relaxation frequency of second process $f_r^{(1)}$ decreases with decreasing temperature from 1 HHz very far from phase transition (100 ^{0}C) to ~50 MHz at T=83.9 ^{0}C, that corresponds to transition into fog phase for investigated CM sample. Using the parameters of relaxation processes obtained from temperature dependence of hypersonic velocity we calculated a contribution of second relaxation process to hypersonic absorption from Eq.(1), shape of function $B_1(T)$ obtained from dispersion of sound velocity. The results of calculation are presented in Figure 2 by solid line for 4.5 HHz. In limits of experimental errors one can say about a satisfactory agreement between calculated and experimentally obtained values of $\alpha\lambda$ for frequencies of 1.1 HHz and 4.5 HHz when the existence of two relaxation processes is assumed in hypersonic frequency range. Significant dependence of relaxation frequency for second process on closeness to the temperature of phase transition indicates its connection with critical fluctuations.

To find out the nature of such fluctuations we carried out an investigation of ultrasound absorption over the frequency range from 2 to 22 MHz.

In nematic liquid crystals for ultrasound range the basic contribution to absorption and dispersion of sound velocity is due to fluctuations of short - range orientation order [11,7]. In CM these fluctuations should also appear. Dispersion of sound velocity, as it can be seen from Figure 1, has a value, which is not more than 1% over the investigated region. It does not allow to make any calculations of relaxation time using Eq.(6). At the same time, the absorption of ultrasound increases noticeably for each frequency. To analyze the absorption using Eq.(5) it is necessary to determine α_{exc}, i.e. absorption caused by order parameter fluctuations. For this purpose, we subtracted the contribution connected with first and second relaxation processes in

hypersonic frequency range from experimentally obtained values of $\alpha\lambda$ for each ultrasound frequency and temperature.

Temperature dependencies of $(\alpha\lambda)_{exc}$ for each ultrasound frequency obtained by such method are presented in Figure 4.

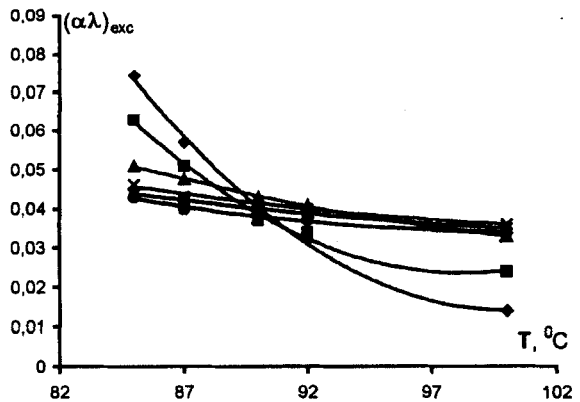

FIGURE 4

Temperature dependence of the excess of absorption $(\alpha\lambda)_{exc}$ of ultrasound in isotropic phase of Cholesteryl Myristate.
(♦-2 MHz, ■-3 MHz, ▲-5.4 MHz, ×-9 MHz, *-16 MHz, • - 22 MHz)

To determine function $B_2(T)$ connected with fluctuation part of heat capacity which appears as a result of existence of order parameter fluctuations [6], and also to determine relaxation frequency $f_r^{(2)}$ of order parameters fluctuation in isotropic phase of CM, we made use of graphic method described in [7].

We plotted the dependence of $(\alpha\lambda)_{exc}$ on f for each temperature and assumed that the shape of function $F_1(f_r/f)$ is identical to that for isotropic phase of nematics. By combination of the graphs of the dependence of $(\alpha\lambda)_{exc}$ on f with the shape of $F_1(f_r/f)$ until the best coincidence [7] we determined $B_2(T)$ and $f_r^{(2)}$ for each temperature

point. Figure 5 presents the obtained results for $B_2(T)$ and $f_r^{(2)}$. The value of relaxation frequency for order parameter fluctuations decreases in CM from 3 MHz (at 100 ^{0}C) to 300 KHz (at 84 ^{0}C). It coincides with our evaluations made on the base of results obtained from spectra of light scattering [4].

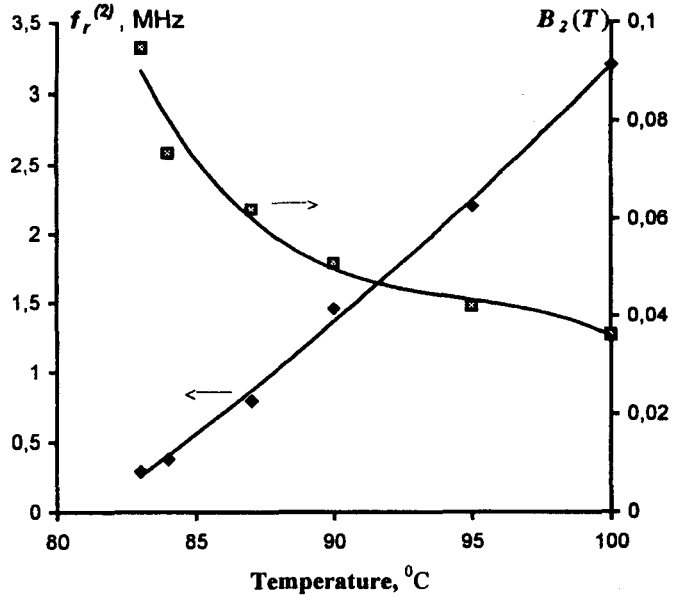

FIGURE 5

Temperature dependence of $B_2(T)$ and $f_r^{(2)}$ in isotropic phase of Cholesteryl Myristate.

From obtained values for $B_2(T)$ and $f_r^{(2)}$ we calculated the values of ultrasound velocity for 2 MHz and 22 HHz using the shape of function F_1 (f_r/f). The results are presented in Figure 1 by solid lines for ultrasound frequencies. As it can be seen from Figure 1,

the calculated values are in good agreement with experimental results for ultrasound velocities. Using the determination of $B(T)=\Delta C_p/C_p^0$, where ΔC_p is the contribution to heat capacity connected with fluctuations, and C_p^0 is regular part of heart capacity, we can write

$$B(T) = \frac{\Delta C_p^1 + \Delta C_p^2}{C_p^0} = \frac{\Delta C_p^1}{C_p^0} + \frac{\Delta C_p^2}{C_p^0} = B_1(T) + B_2(T)$$

Here ΔC_p^1 is a part of heart capacity connected with fluctuations which are responsible for second relaxation process (hypersound), and ΔC_p^2 is part of heat capacity connected with order parameter fluctuations (ultrasound). The results of measurements of molar heat capacity for CM from solid state until isotropic phase are presented in [13].

They allow to calculate the values of $B(T)$. Table 2 presents the values of $B_1(T)$, $B_2(T)$, $B_1(T)+B_2(T)$ which were obtained by us and the values of $B(T)$ calculated on the base of results presented in [13].

By comparison of two last columns in the table one can say about good agreement between the values of $B(T)$ obtained by analysis of sound propagation in isotropic phase of CM and the values of $B(T)$ calculated from the results of heat capacity measurements.

TABLE 2

T (°C)	$B_1(T)$	$B_2(T)$	$B_1(T) + B_2(T)$	B(T)
85	0.07	0.075	0.145	0.170
90	0.05	0.05	0.100	0.100
95	0.04	0.043	0.083	0.082
100	0.025	0.036	0.061	0.056

Thus, it can be assumed that for CM in the frequency range from 2 MHz to 7 HHz, at least three relaxation processes take place.

First relaxation process which has weak temperature dependence over the frequency range 1-7 HHz and third one (characterized by strong dependence on approaching the phase transition) over the frequency range 2-22 MHz connected with order parameter fluctuations, are analogous to those observed in the isotropic phase of nematic MBBA [11]. Second relaxation process is characteristic only for isotropic phase of CM and it is not observed for nematics.

The existence of this relaxation process is probably connected with the kinetics of structure fluctuations either smectic or cholesteric type. This assumption can be confirmed by temperature behavior of inverse integral intensity of scattered light in the isotropic phase of CM [4]. For inverse integral intensity in isotropic phase of CM over the temperature range (89 - 84)^{0}C the significant deviation from linear dependence, predicted by De Gennes [14] for order parameter fluctuations of nematic type, is observed. Such deviation may appear as a result of the development of additional structure fluctuations (smectic or cholesteric) which were theoretically considered in [3] for isotropic phase of nematics also possessing smectic mesomorphic phase.

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