

Uniaxial-to-biaxial cholesteric and nematic phase transitions on a lyotropic alcohol-free mixture

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Interferometric measurements of the chirality-induced biaxiality in the vicinity of the uniaxial-to-biaxial cholesteric transition of the lyotropic system potassium laurate, decylammonium chloride, H_2O , and brucine sulfate are reported. The mean-field approach to describe the cholesteric-to-cholesteric transition allows an estimate of the ratio between coefficients of the Landau expansion. The values of the bare correlation length, $\xi_0 \sim 1000 \text{ \AA}$, calculated are larger than in lyotropic systems with alcohol. The chirality-induced biaxiality measurements in the limit of zero elastic field ($q^2=0$) and the birefringence measurements in the nematic phase confirm critical properties of the uniaxial-to-biaxial nematic transition. The critical exponents for the order parameter (β) and the susceptibility (γ) are in good agreement with the values calculated for the XY model.

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I. INTRODUCTION

Phase transitions [1] are one of the most interesting areas of condensed-matter physics. For many years scientists have been interested in investigating the properties of matter near critical points and along the phase-transition boundaries. In particular, lyotropic liquid crystals present many different phases as a function of temperature and the relative concentrations of amphiphilic molecules and their solvent. We will focus our attention on the nematic and cholesteric phases.

The phase diagram of lyotropic nematic liquid crystals is very rich [2,3]: Two uniaxial nematic phases ($N-C$, calamitic, and $N-D$, discotic) and a biaxial nematic phase ($N-B$) were identified. In 1983, Galerne and Marcerou [4] reported interferometric measurements of the optical birefringence of the potassium laurate (KL)-decanol (DeOH)-water lyotropic system, concluding that the transitions from the uniaxial to the biaxial phase are mean-field second-order transitions. More recently, Melnik, Photinos, and Saupe [5] studied the critical properties of the second-order uniaxial-biaxial transition of the same lyotropic system on surface and magnetic-field-aligned samples. They observed deviations from mean-field behavior in a 20-mK range below the transition to $N-D$ and in a temperature range of at least the same extent above the transition to $N-B$. The values obtained for the critical exponents of the order parameter (β) and susceptibility (γ) in the uniaxial range are in good agreement with the values calculated for the XY model.

The phase diagrams of lyotropic cholesteric liquid crystals [6–8] also present three different phases, which were classified as $Ch-D$, $Ch-B$, and $Ch-C$, referring to the nematic classification. As the $Ch-D$ and $Ch-B$ phases have the same symmetry [9], they cannot transform to each other via second-order phase transitions (similar to the liquid-gas transition). In a previous work [10] we reported interferometric measurements of the chirality-induced biaxiality in the vicinity of the $Ch-D$ - $Ch-B$ phase transition, performed in lyotropic mixtures of KL-

DeOH-water with different chiral agents. The measurements show that the uniaxial-to-biaxial cholesteric phase transition is not second order, as it is in lyotropic nematic liquid crystals and is not first order either. There is no transition as in the liquid-gas phase diagram beyond the critical point.

In this paper we report interferometric measurements of the chirality-induced biaxiality in the $Ch-D$ - $Ch-B$ transition, performed in a lyotropic system composed by KL-decylammonium chloride (DaCl)-water-brucine sulfate. This alcohol-free mixture [11] has the advantage of chemical stability compared to the alcohol-containing mixtures. The analysis of the birefringence curves as a function of temperature allowed us to determine relations between the Landau coefficients of the free-energy-density expansion. Close to the transition, the susceptibility of the biaxial order parameter diverges and, consequently, the chiral field-induced biaxiality increases considerably. As the chiral field is a particular case of an elastic field, our measurements of the critical exponent γ in the limit as the cholesteric pitch (P) goes to infinity [i.e., $q = (2\pi/P) \rightarrow 0$, being a nematic phase] also allow a discussion of the $N-D$ - $N-B$ transition.

II. THEORY

Following Landau-de Gennes theory [12], the free-energy density of the cholesteric phase may be expanded in terms of $Q_{\alpha\beta}$ (second-order tensor, order parameter) and its gradients. To the lowest order, the contribution of the gradients to the free energy is [12]

$$F_{\nabla} = L_0 \epsilon_{\alpha\beta\gamma} Q_{\gamma\delta} \nabla_{\alpha} Q_{\beta\delta} + \frac{1}{2} L_1 \nabla_{\alpha} Q_{\beta\gamma} \nabla_{\alpha} Q_{\beta\gamma} + \frac{1}{2} L_2 \nabla_{\alpha} Q_{\alpha\beta} \nabla_{\gamma} Q_{\gamma\beta} . \quad (1)$$

In the cholesteric configuration with the chiral axis along the 1 axis, F_{∇} reduces to [10]

$$F_{\nabla} \sim -L_1 S q^2 \xi , \quad (2)$$

with $q = -L_0/2L_1$, S is the usual order parameter of the uniaxial nematic phases, and ζ is the scalar order parameter specific to the biaxial phase.

The total free-energy density of the cholesteric phase at the uniaxial-biaxial transition takes the usual Landau form:

$$F = \frac{1}{2}a(T)\zeta^2 + \frac{1}{4}b\zeta^4 - cq^2\zeta, \quad (3)$$

where $a(T) = a_0(T - T_c)$, T_c is the uniaxial-biaxial transition temperature, and q^2 is the chirality field in interaction with ζ . As $S \sim 1$, $c = L_1S = KS$ is of the order of magnitude of K , the Frank elastic constant.

The correlation length $\xi = \xi_0(\Delta T/T_c)^{-1/2}$ of the biaxial order parameter in the uniaxial phase can be written as [10,12]

$$\xi = \left[\frac{c}{|a_0|T_c} \right]^{1/2} \left[\frac{\Delta T}{T_c} \right]^{-1/2}. \quad (4)$$

It is well known [12] that the orientational order parameter of nematic liquid crystals undergoes field-induced modifications, which can be observed by means of the changes of the optical indices. In the case of an elastic field, the field-induced modifications of the order parameter essentially arise from the molecular interaction. A simple example of elastic field is given by the chiral field present in cholesteric liquid crystals. The cholesteric liquid crystal may be regarded as a usual nematic liquid crystal submitted to a chiral elastic field. The chiral elastic field introduces differences between the directions perpendicular to the director, and thus causes biaxiality to appear. This effect was predicted by Priest and Lubensky [13] and measured in thermotropic [14] and lyotropic [10] liquid crystals.

In first approximation, and in analogy with the usual definition of the Cotton-Mouton constant [5,12], we may define a "cholesteric susceptibility" as

$$\eta = \left. \frac{\partial \bar{s}(q)}{\partial q^2} \right|_{q^2=0} \quad (5)$$

and also a "constant" for the elastic-field-induced biaxiality

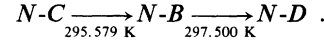
$$C = A \frac{\Delta(n_2 - n_1)}{q^2}, \quad (6)$$

where $\bar{s}(q)$ is the thermal average of the order parameter (function of q) [15], $n_2 - n_1$ is the usual birefringence and A is a constant.

The behavior of the birefringence as a function of the temperature around the $N-D-N-B$ transition is well known [4,5]: $n_2 - n_1 \neq 0$ at the $N-B$ phase and goes to zero at T_c (the transition temperature). When the nematic phase is doped with chiral molecules, the birefringence curves as a function of temperature [10] are rounded off around T_c , which can be interpreted as the chirality-induced biaxiality.

III. EXPERIMENT

The nematic sample [11] is a mixture of KL-DaCl-water (H_2O), with the concentration in weight percent 33.5 wt % - 4.1-62.4, respectively. The phase sequence as a function of the temperature is



A chirality field of different strengths is realized by dissolving increasing amounts of brucine sulfate heptahydrate (BS) into the nematic sample. The samples concentrations are shown in Table I. A nearly constant weight ratio, $\mathcal{W}(\text{KL}):\mathcal{W}(\text{DaCl}):\mathcal{W}(\text{H}_2\text{O}) \cong 1:0.1224:1.8615$, was used and different amounts of BS were added.

The phase diagrams [7,16] of lyotropic cholesteric liquid crystals (with BS) have a complex topology. For large amounts of BS [weight ratio $\mathcal{W}(\text{BS})/\mathcal{W}(\text{KL}) = W$ about 0.05 in samples with decanol], only the Ch- D phase is observed [16]. For decreasing values of W (< 0.03), the Ch- B and Ch- C phases appear as a function of temperature. Depending upon the particular region of the phase diagram, the transition temperature can change by several degrees as a function of W . For very small BS dopings ($W \lesssim 10^{-2}$) important changes in the transition temperatures are not expected as a function W [17]. To avoid important drifts to the transition temperatures, we restrict ourselves to small doping concentrations of BS ($0.0051 < W < 0.0132$). If more BS is introduced in the nematic phase, the phase sequence could drastically change, as discussed before. A small quantity of ferrofluids [6] (less than 1 μl in 2.5 ml of the lyotropic mixture) is also added to the samples in order to help their orientation in the presence of a weak magnetic field ($H \sim 100 \text{ G}$).

The samples are encapsulated inside microslides of 0.1 and 0.2 mm thickness, placed in an INSTEC HS1-i hot stage system positioned in a Leitz orthoplan-pol microscope. The smallest temperature steps used were 5 mK and the temperature was kept constant to about 2 mK.

Nematic samples (discotic and biaxial) were aligned by the combination of a small magnetic field and the walls of the microslide. With this procedure, a homogeneous pseudoisotropic texture is obtained in the $N-D$ phase with the director parallel to the light propagation direction and, after the transition to the $N-B$ phase, a homogeneous planar texture is achieved. The birefringence is measured with a Berek compensator.

Cholesteric samples are aligned [6] with the small magnetic field (H) in the Ch- D phase. The texture observed in the polarizing microscope shows black stripes which cor-

TABLE I. Sample compositions in weight ratio of KL:DaCl:H₂O:BS. N represents the nematic sample. S represents the cholesteric samples.

Sample	Weight ratio KL:DaCl:H ₂ O:BS
N	1:0.1224:1.8627:0
S1	1:0.1222:1.8613:0.0051
S2	1:0.1224:1.8611:0.0096
S3	1:0.1226:1.8610:0.0132

respond to the cholesteric planes homeotropically oriented.

The experimental setup is presented in detail in Ref. [10]. \mathbf{H} is at 45° from the polarizer and the microscope gives the image of the sample in the plane of a narrow slit parallel to the stripes. A photomultiplier measures the light intensity of the interference pattern ($\lambda=5460 \text{ \AA}$) sampled by the slit. The intensity of the light is measured [10] as a function of the distance (X) from the homeotropic stripe and, after normalization, is compared to the expression

$$I = I_0 \sin^2[(\pi D / \lambda) \Delta n \sin^2 q x], \quad (7)$$

where D is the sample thickness, $\Delta n (=n_3 - n_2)$ is the birefringence, and I_0 is a constant (Ch- D phase, constant temperature). After that, the slit is placed on the homeotropic stripe and the intensity is measured as a function of the temperature. The measurements are described by the equation

$$I = I_0 \sin^2[(\pi D / \lambda) \delta n], \quad (8)$$

where $\delta n = n_2 - n_1$ is the biaxiality. With the convenient normalization, the order parameter ζ is written as $\zeta = \delta n / \Delta n$ [Δn at Ch- D phase is obtained using expression (7)].

IV. RESULTS AND DISCUSSION

Figure 1 shows the zero-field normalized birefringence ζ [$=(\delta n / \Delta n_c)$, where Δn_c is the birefringence at the N-C phase] as a function of T . Figure 2 shows a log-log plot of the data of Fig. 1 in the biaxial range near T_c , made to determine the critical exponent of the order parameter. As an average of a series of measurements, we obtained

$$T_c = 297.500 \text{ K}, \quad \beta = 0.38 \pm 0.02.$$

We estimate the change in β due to changes in T_c : for $T_c \pm 0.01 \text{ K}$ we obtained $\beta \pm 0.02$. Figure 3 shows the square of the order parameter as a function of temperature (ζ^2 vs T) across the Ch- D –Ch- B transition of the nematic (zero-field) sample and three different cholesteric samples. Special care was taken to reach an equilibrium

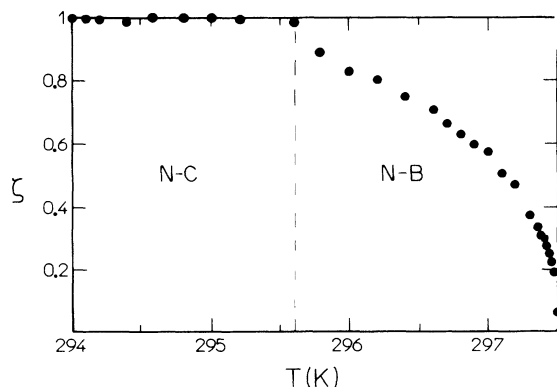


FIG. 1. Zero-field normalized birefringence as a function of temperature. Nematic sample.

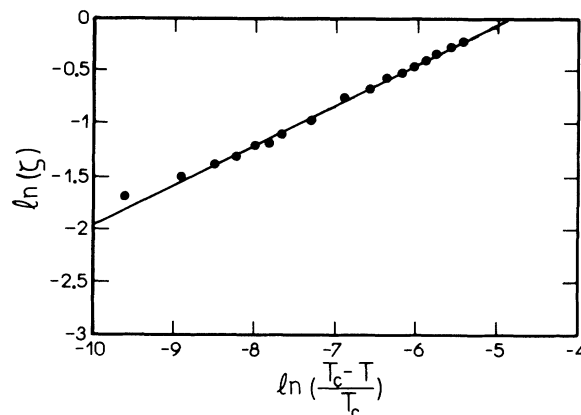


FIG. 2. Double logarithmic plot of zero-field birefringence as a function of the reduced temperature $[(T_c - T)/T_c]$. The solid line is the best fit with adjusted values of T_c and β .

state before each measurement. After the temperature is changed between each point, a waiting period of about 20 min. follows.

The squared biaxial order parameter versus temperature data present two asymptotical behaviors far from the transition: $\zeta = 0$ in the Ch- D phase, and $\zeta^2 = -(a_0/b)(T - T_c)$ in the Ch- B phase. Close to T_c , the data present a rounding off which is due to the chirality-induced biaxiality. From the minimization of Eq. (3), a theoretical function $\zeta^2(T)$ is obtained and can be fitted to the experimental data. A typical fit is shown in Fig. 4. The quality of this fit, made in a large temperature range around T_c ($\Delta T \sim 1 \text{ K}$ and $\Delta T/T_c \sim 4 \times 10^{-3}$), indicates that reasonable estimations of the ratios between the Landau coefficients can be obtained. This fit, however, it is not enough to determine the critical exponents. We will return to this point later on. The ratios between the Landau coefficients of Eq. (3) determined from the fit are presented in Table II, where each cholesteric phase is identified by the symbols S1, S2, and S3.

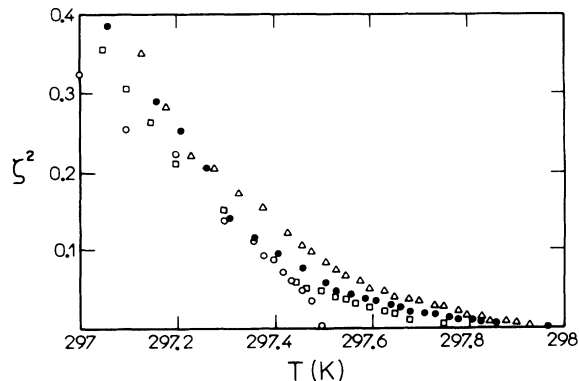


FIG. 3. Squared order parameter as a function of temperature near the uniaxial to the biaxial transition, at various chiral elastic fields: \circ , nematic sample—zero field; \square , cholesteric sample S1; \bullet , cholesteric sample S2; \triangle , cholesteric sample S3.

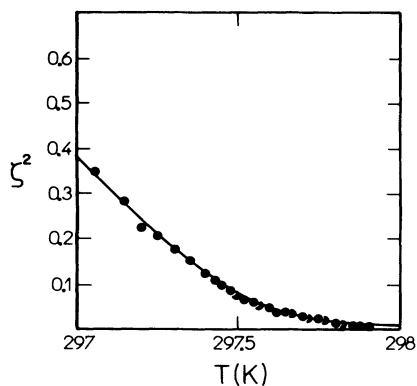


FIG. 4. Squared order parameter vs temperature, across the Ch-*D*–Ch-*B* transition, sample S3. The solid line is a fit to the theoretical function.

The ratios b/a_0 and c/a_0 show the expected behaviors assumed in mean-field theories being almost constant. The small variations observed could be due to the different relative concentrations in each sample. It is interesting to compare our values of b/a_0 (of cholesteric samples) with the values obtained in lyotropic nematic liquid crystals [18] (KL-DeOH- D_2O mixture): our values are about 10^{-2} smaller than the nematic values. Besides the fact that we are studying cholesteric liquid crystals, another difference between the two lyotropic mixtures is the presence of DaCl in our system, in place of DeOH. These two aspects could be responsible for the large difference between the two systems. Another point that has to be considered in this comparison is the difference between the amphiphilic concentrations of the nematic described in Ref. [18] and ours: KL and DeOH have concentrations of about 25 and 6 wt. % in Melnik, Photinos, and Saupe's work and we have KL \sim 33 wt. % and DaCl 4 wt. %.

The ratio cq^2/a_0 (Table II) is about the same for samples S1 and S2 and increases for increasing values of q^2 (S3). The measured values of the induced biaxiality c/a_0 correspond to about 10^{-7} cm² K. This value is about 10^3 larger than the values obtained [10] in cholesterics with DeOH in place of DaCl. These results may also be compared to measurements of K/a_0 available in the literature. The magnetically induced biaxiality at *N-D*–*N-B* transition in a KL-DeOH- D_2O system could be evaluated [19,20] as 3×10^{-9} cm² K. Another measurement of K/a_0 in the same nematic mixture obtained by light-scattering measurements gave [21] $\sim 10^{-8}$ cm² K. Our results indicate that the chirality-induced

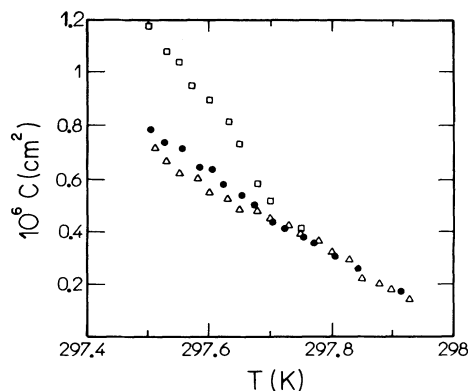


FIG. 5. Cholesteric susceptibility $C = \xi/q^2$ as a function of temperature. Cholesteric samples: S1 (\square); S2 (\bullet); S3 (\triangle).

biaxiality is larger in cholesteric liquid crystals with DaCl and even higher than the magnetically induced biaxiality in nematic liquid crystals with DeOH.

Using our values of c/a_0 and T_c in Eq. (4), we can calculate the bare correlation length ξ_0 of the biaxial order parameter (Table II). These values of ξ_0 are larger than the typical micellar dimensions [6] (about 100 Å) and are also larger than the values obtained in the lyotropic mixtures with DeOH.

As discussed before, the chiral field is a simple example of the elastic field, and our measurements of the chirality-induced birefringence in cholesteric liquid crystals could be used to investigate the critical properties of the uniaxial-biaxial transition in nematic liquid crystals ($q^2 \rightarrow 0$). From the data shown in Fig. 3, the induced biaxiality $\Delta(n_2 - n_1) = \delta n$ can be obtained straightforwardly in the Ch-*D* phase [22]. We will restrict our analysis to the discotic range, i.e., $T > T_c$. In the biaxial range, the induced biaxiality seems to be not proportional to q^2 . A similar result was obtained [5] by Melnik, Photinos, and Saupe using a magnetic field.

Figures 5 and 6 show the cholesteric susceptibility $C = \xi/q^2$ and C^{-1} as a function of temperature. The data were derived from Fig. 3 in the Ch-*D* range. In this analysis, we assumed that T_c in the cholesteric-to-cholesteric transition is the same obtained before at the nematic-to-nematic (i.e., $q = 0$) transition: $T_c = 297.500$ K. This assumption can be justified by two reasons: (i) observing the texture of the cholesteric samples in the optical microscope, we note changes in the homeotropic regions of the Ch-*D* phase for $T < T_c$ (in the Ch-*B* phase there are no homeotropic regions [3]); (ii) the BS doping is very small, with $W < 0.014$ and in this limit, as dis-

TABLE II. Birefringence in the Ch-*D* phase (Δn); pitch (P) and $q = 2\pi/P$; ratios between the coefficients of Landau expansion and bare correlation length (ξ_0) of the cholesteric samples.

Sample	$10^3 \Delta n$ (Ch- <i>D</i>)	P (μm)	$10^{-2} q^2$ (cm^{-2})	b/a_0 (K)	$10^2 cq^2/a_0$ (K)	$10^{-9} c/a_0$ ($\text{\AA}^2 \text{K}$)	ξ_0 (\AA)
S1	1.7 ± 0.1	145.9 ± 0.2	1852 ± 4	-1.25 ± 0.03	2.1 ± 0.4	1.1 ± 0.2	1923 ± 175
S2	2.2 ± 0.3	123.3 ± 0.2	2609 ± 6	-1.35 ± 0.05	2.2 ± 0.5	0.8 ± 0.2	1640 ± 202
S3	2.3 ± 0.4	97.9 ± 0.2	4111 ± 1	-1.25 ± 0.05	5.9 ± 0.6	1.4 ± 0.1	2169 ± 78

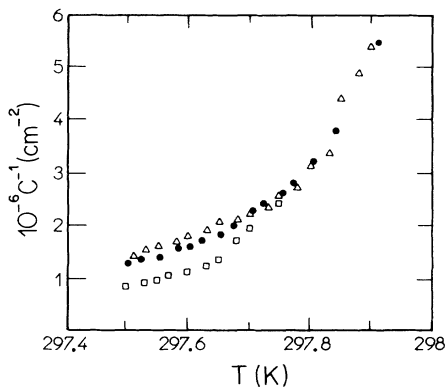


FIG. 6. Inverse of the cholesteric susceptibility $C^{-1}=q^2/\zeta$, as a function of temperature. Cholesteric samples: S1 (\square); S2 (\bullet); S3 (Δ).

cussed before, we do not expect drastic changes in T_c due to this addition of BS. Figure 6 shows that deviations from the linear behavior are observed particularly near T_c . These deviations are more important for increasing values of q^2 . In the limit of low q^2 and at about 0.2 K above T_c , the linear behavior is more defined. These behaviors are essentially the same observed by Melnik, Photinos, and Saupe [5] using magnetic fields.

Figure 7 shows a plot using the data the Fig. 6 for the determination of the susceptibility exponent γ . The average value for γ obtained from a series of measurements is

$$\gamma = 1.35 \pm 0.15.$$

Our results indicate that deviations from the mean-field theory exist in temperature ranges around T_c corresponding to $\Delta T/T_c \sim 10^{-4}$ [23]. As the experimental data very close to T_c are not used in the fit to determine γ , this exponent is not particularly sensitive to changes in T_c . We estimate that for $T_c \pm 0.1$ K, the variation in γ is less than 0.05.

The chirality-induced biaxiality measured close to T_c could allow an estimate of the exponent of the critical isotherm (δ). In our case, however, we cannot have many different curves of ζ vs T for different q^2 because by increasing the brucine doping important drifts of T_c are observed and even the topology of the phase diagram changes. This exponent, however, is very sensitive to changes in T_c . In these conditions, the data extracted

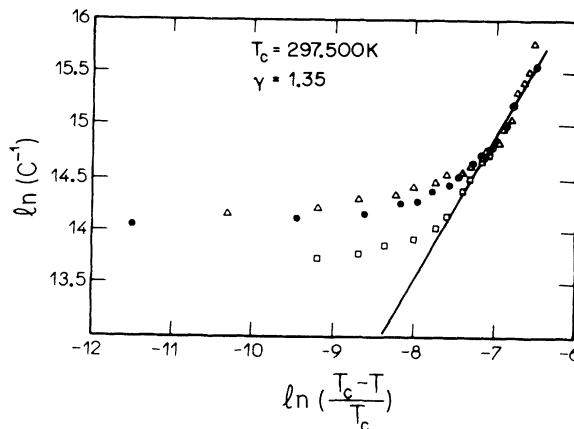


FIG. 7. Double logarithmic plot of C^{-1} vs the reduced temperature $[(T_c - T)/T_c]$ with the best linear fit. Data from Fig. 6, Ch-D range.

from Fig. 3 are not enough to determine δ with an acceptable accuracy.

V. CONCLUSIONS

The mean-field approach to describe the Ch-D-Ch-B transition (in the temperature range around T_c corresponding to $\Delta T/T_c \sim 4 \times 10^{-3}$) allows an estimate of the ratio between the Landau coefficients of the alcohol-free lyotropic mixture. The results obtained lead to values of ξ_0 greater than the usual bare correlation length of lyotropic liquid crystals with DeOH. The measurements confirm that from the Ch-D phase to the Ch-B phase, the system does not cross transition lines in the phase diagram, similar to the liquid-gas transition after the critical point. This result was theoretically predicted [9] and experimentally observed [10] in lyotropic liquid crystals with DeOH.

The results on the uniaxial-biaxial alcohol-free lyotropic nematic liquid crystals (a cholesteric liquid crystal with $q^2=0$) confirm the critical properties [5] of this transition. The critical exponents for the order parameter and for the susceptibility obtained from analysis of the experimental data agree with the theoretical results [24] for XY model, $\beta=0.38$ and $\gamma=1.35$. Deviations from the mean-field theory exist in temperature ranges around T_c corresponding to $\Delta T/T_c \sim 10^{-4}$.

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