

# The Influence of Structural Features of Molecules on Viscosity Characteristics, on Dynamic of Orientation Processes and Structural Ordering in Liquid Crystal Systems

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**Abstract.** The possible transitions between smectic A (SmA), Sm C, Sm C\* and the nematic phases (N), viscosity and orientation processes were studied in liquid crystals (LC) and LC systems during and in the vicinity of the  $N LC \leftrightarrow Sm LC$  phase transition. Investigation of structural and dynamic aspects of liquid crystalline mesophases were carried out by ESR relaxation induced by spin probes. The values of the viscosity coefficient in the mesophase were estimated. The dependence of the viscosity coefficient on the structural features of molecules of the components of the studied systems was established. Based on the obtained experimental and theoretically calculated data, as well as on the conducted explanatory theoretical analyses, it was shown that in the studied LC systems the  $N^* LC \rightarrow IL$  phase transition was apparently best described as a combined phase transition, close to the Lifshitz' tricritical point, which occurs in the systems with short-range interactions of molecules.

**Keywords:** smectic and ferroelectric liquid crystals, molecular structure, phase transition, ESR relaxation, molecular interactions, correlation time, viscosity.

## 1. Introduction

The aim of the study was to obtain numerical values of such dynamic parameters, as orientation relaxation time and ordering, viscosity and pre-translational phenomena in liquid crystals (LC) and LC systems, which would offer new technical solutions with the potential to expand the field of practical applications of LC. Physical processes in liquid crystals (LC) in the vicinity of the phase transition nematic liquid crystal (NLC)  $\leftrightarrow$  smectic liquid crystal (SmLC) have been intensively studied theoretically and experimentally [1–5].

The liquid crystalline state of matter is of interest to researchers for two reasons. The first is practical – due to the high optical sensitivity of LC to a change in the electric field with an extremely low control voltage and low power consumption. The second reason is the extraordinary variety of physical effects in LCs, which is a consequence of their structure. However, many questions have not been answered; for example, the nature of the  $NLC \rightarrow SmLC$  phase transition, and the viscosity change close to the phase transition has not been established.

The microscopic theory of Kobayashi and McMillan [6], based on the self-consistent field theory, indicates the dependence of the nature of the  $NLC \rightarrow SmLC$  phase transition on the

width of the temperature range ( $\Delta_{NSm}$ ) of the nematic phase. Also according to that theory, the magnitude of  $\Delta_{NSm}$  depends on the ratio of the longitudinal and transverse sizes of LC molecules. Moreover, in liquid crystals with a wide temperature range of the nematic phase:  $\Delta_{NSm} = 1 - \frac{T_{NSm}}{T_{NI}} > 0.12$ , where  $T_{NSm}$  – is the temperature of the  $NLC \rightarrow SmLC$  phase transition,  $T_{NI}$  – is the temperature of the  $NLC \leftrightarrow IL$  (isotropic liquid) phase transition, the  $NLC \rightarrow SmLC$  phase transition of the second-order is observed [6]. With the increase of molecules' length, the entropy of the phase transition also increases, while the temperature interval of the nematic phase decreases, and the  $NLC \rightarrow SmLC$  phase transformation becomes the first-order phase transition. Moreover, the  $NLC \rightarrow SmLC$  phase transition is not continuous, but at least, always remains a weakly expressed first-order transition, which is due to the strong connection between the nematic and smectic order parameters. However, if the characteristic features inherent to a first-order phase transition (the density leap and the latent heat leap) are weakly expressed, then the  $NLC \rightarrow SmLC$  phase transition can be considered as a second-order phase transition. With increasing of pressure in the vicinity of the phase transition the fluctuations of orientation decrease, and when the certain critical pressure is reached, the first-order phase transition is transformed into a second-order phase transition [7]. The pre-transition phenomena observed near the  $NLC \rightarrow SmLC$  phase transition are associated with the fluctuations of the smectic order parameter  $S_{Sm}$ . During the first-order phase transition, the value of  $S_{Sm}$  should sharply decrease to zero when the temperature  $T_{NSm}$  is reached. In the case of a second-order phase transition, the parameter  $S_{Sm}$  decreases monotonically as the temperature approaches the phase transition temperature from below. The application of the Landau phenomenological theory, where the free energy is presented in the same form as in the Landau–Ginsburg theory of superconductivity, and the vector potential is replaced by the director of the nematic, allows one to describe the distortions of the smectic order parameter and the orientation of molecules in the vicinity of the phase transition temperature [8]. The difference between the McMillan [6] and De Gennes [8] approach is that McMillan describes the temperature dependence of the correlation length  $\zeta$  by the expression  $\zeta \sim (T - T_{NA})^{-\nu}$ , where in accordance with the mean field theory critical index  $\nu = 0.5$ . De Gennes considered the behavior of the smectic order parameter in the vicinity of the  $NLC \rightarrow SmLC$  phase transition based on the similarity theory and found that the critical index  $\nu = 2/3$ .

The present work is devoted to the study of possible transitions between  $Sm A$ ,  $Sm C$  and the nematic phase ( $N$ ), viscosity and orientation processes in LC and LC' systems during and in the vicinity of the  $NLC \rightarrow SmLC$  phase transition. Experimentally, many of these transitions turn out to be first-order phase transitions. However, from the point of view of the Landau rules [9], all of them can be second-order transitions. Although these transitions of the second-order are less common, they are of great interest because they are always accompanied by pre-transitional anomalies. The appearance in the nematic phase of quasi-smectic features can lead to sharp changes in some important constants (elastic constants, transport properties, etc.).

## 2. Experimental Technique and Research Objects

Viscosity and ordering of molecules were investigated by electron spin resonance (ESR) technique with the help of spin probe (Fig.1) in such smectic LC, as  $C_5H_{11}O-(OH)C_6H_3-CH=N-C_6H_4-C_5H_{11}$  {A},  $C_8H_{17}O-C_6H_4-N=N-C_6H_4-C_9H_{19}$  {B} and ferroelectric smectic  $C^*$  LC:  $C_8H_{15}O-C_6H_4-C_6H_4-COO-CH_2-C^*H(CH_3)-C_2H_5$  {C} ( $Cr^{42.5^{\circ}C}$   $SmC^{*43^{\circ}C}$   $SmA^{64.5^{\circ}C}$   $IL$ );  $C_8H_{17}O-C_6H_4-C_6H_4-CH_2-CH_2-C^*H(CH_3)-C_2H_5$  {D} ( $Cr^{46^{\circ}C}$   $SmI^{60.5^{\circ}C}$   $SmH^{65.5^{\circ}C}$   $SmC^{*67^{\circ}C}$   $IL$ ). The {A/C}, {A/D}, {B/C}, {B/D} systems with different concentration of components were also studied with the abovementioned technique. Note that the studied LC systems have  $\approx 10$  times greater spontaneous polarization and a wider temperature range for the existence of the ferroelectric phase than {C} and {D} LC. What is of practical interest.

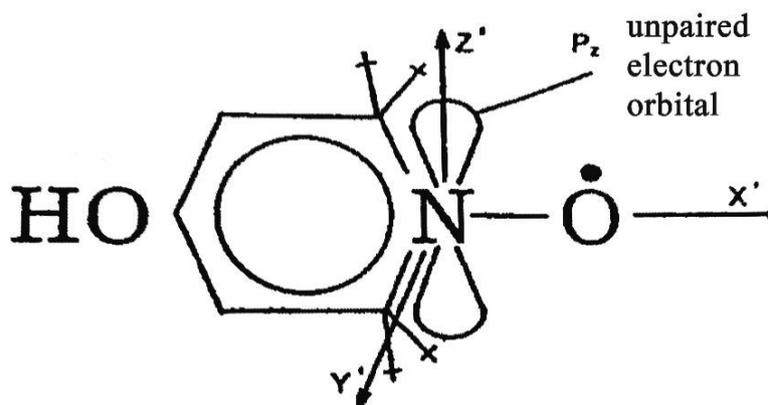


Fig. 1. Structural Formula of Nitroxyl Radical

ESR measurements were carried out on a radio spectrometer P $\Theta$ -1301 in a microwave region of 9 GHz. To avoid the distortion of line shape, the amplitude of the high frequency modulation was set to be several times smaller than the line width, and the microwave power was chosen to be so small that the ESR signal was far from saturation. The magnetic parameters were measured with an accuracy of  $\pm 0.4$  G. To minimize line broadening, due to the dipole – dipole interaction between the molecules of the spin probe, the concentration of the radical was determined to be as low as  $\sim 10^{-4}$  mol/l.

The samples under study were prepared by thoroughly mixing the LC components in the isotropic phase to obtain a homogeneous solution of the system. Uniformly oriented samples

were obtained by the application of a sufficiently strong magnetic field  $\sim 3000\text{ G}$ . During the experiment, the samples were heated by a hot air stream, blowing through a quartz tube passing through the resonator of the spectrometer. The accuracy of temperature measurement was  $\pm 0.05^\circ\text{C}$ .

Our analysis of the ESR spectra was based on well-developed theory of spin relaxation [10–12]. According to this theory, the width of spectra  $T(m)^{-1}$  is defined by the equation [10, 13]:

$$T(m)^{-1} = L + Bm + Cm^2 \quad (1)$$

where,  $m = -1, 0, +1$  – is nuclear quantum number characterizing the hyperfine splitting component; parameters  $L, B, C$  depend on the magnitude of magnetic anisotropy and the rate of molecular reorientation.

To simplify the analysis of ESR spectra, it is assumed that the rotational diffusion tensor is axially symmetric. The laboratory coordinate system  $(X, Y, Z)$  is chosen so that the  $Z$  – is the axis of symmetry and is directed by director.  $X, Y$  – axes are in the plane perpendicular to the  $Z$  – axis. The main values of the hyperfine splitting constant tensor:  $A_{xx} = A_{yy} = A_{\perp}, A_{zz} = A_{\parallel}$ .

$A_{\perp}$  – is the value of the hyperfine splitting constant of the experimental spectrum when magnetic field is normal to the  $Z$  axis;  $A_{\parallel}$  – is the value of the hyperfine splitting constant of the experimental spectrum when magnetic field is directed along the  $Z$  axis. The molecular coordinate system  $(X', Y', Z')$  relates to radical fragment as shown on Fig.1. In this coordinate system  $\hat{A}$  and  $\hat{g}$  tensors can be considered diagonal [14].  $A_{x'x'} = 31\text{ G}, A_{y'y'} = 5.2\text{ G}, A_{z'z'} = 5.2\text{ G}$  – are the main values of the hyperfine splitting constant of radical in the molecular coordinate system.

For further calculations, it is necessary to establish the orientation of  $Z$  – axis on the molecular coordinate system  $(X', Y', Z')$ . The idea of solving this problem is to compare the theoretically calculated ratio  $B/C$  with the experimentally derived (based on the analysis of line width) value  $(B/C)_{\text{exp}}$ . The  $B/C$  calculation results and their corresponding  $(B/C)_{\text{exp}}$  experimental values are shown in Table1.  $(B/C)_{\text{exp}}$  is observed to best coincide with the corresponding calculated value for the case when the  $Z$  – axis of the rotational diffusion tensor coincides with the  $Y'$  – axis of the molecular coordinate system. Small deviations between these quantities, apparently, are associated with various fluctuations, leading to a non-strict coincidence of  $Z$  – and  $Y'$  – axes. Thus, the radical in the LC medium is oriented in such way that the  $Y'$  – axis of the molecular coordinate system becomes parallel to the  $Z$  – axis of the laboratory coordinate system.

**Table 1.** Calculation results of the B/C for the binary systems with different orientations of the rotational diffusion tensor in the molecular coordinate system

Mol %	°C	Z=X'	Z=Y'	Z=Z'
		B/(C) <sub>cal</sub>		
		-2.8176	-2.8187	-2.8976
		(B/C) <sub>exp</sub>		
{B}/{D}20%	27	-4.1973	-2.9406	-3.1415
	34	-4.5418	-2.5314	-2.3231
	40	-3.7732	-2.2983	-1.8567
	48	-2.7745	-2.6425	-2.5452
	51	-2.4585	-2.7811	-2.8224
	55	-2.8617	-2.4958	-2.2518
	60	-3.1865	-2.5956	-2.4514
	65	-2.7249	-3.0632	-3.3865
	70	-1.6876	-3.0431	-3.3464
	76	-1.0607	-2.7095	-2.6793
{D}	81	-1.6153	-2.8427	-2.9456
	39	-4.3435	-2.7102	-2.6806
	42	-4.4758	-2.3309	-1.9220
	47	-3.5923	-2.5238	-2.3079
	50	-2.6600	-2.6317	-2.5236
	55	-2.4904	-2.2633	-1.7868
	61	-2.9475	-2.1973	-1.6548
	64	-3.1721	-2.6452	-2.5505
	66	-2.5711	-2.7603	-2.7807
	70	-1.5251	-2.4958	-2.2517
{B}/{C}(20%)	24	-1.0634	-2.6606	-2.5815
	31	-1.8202	-3.0592	-3.3786
	40	-3.3397	-2.8890	-3.0383
	46	-4.4557	-2.5153	-2.2908
	51	-4.3794	-2.6549	-2.5699
	55	-3.4105	-2.7958	-2.8518
	60	-2.5690	-2.3851	-2.0304
	63	-2.5416	-2.1166	-1.4934
{C}	37	-3.0261	-2.4261	-2.1124
	40	-3.1323	-2.5511	-2.3625
	42	-2.4032	-2.2527	-1.7656
	43	-1.3798	-2.3416	-1.9435
	48	-1.1028	-2.8336	-2.9274
	56	-2.0480	-2.8685	-2.9972
	60	-3.5855	-2.5850	-2.4302
	65	-4.5320	-2.7649	-2.7900
	74	4.2564	-3.0534	-3.3669
{A}/{D}(7%)	28	-3.2332	-2.7452	-2.7505
	33	-2.5033	-2.3786	-2.0173
	40	-2.6086	-2.5662	-2.3926
	42	-3.0932	-2.6719	-2.6040
	46	-3.0667	-2.2848	-1.8298
	50	-2.2259	-2.1803	-1.6208

	55	-1.2566	-2.6083	-2.4767
	60	-1.1789	-2.7344	-2.7291
	65	-2.2938	-2.4857	-2.2316
{A}/{C}(7%)	33	-4.5716	-3.1267	-3.5136
	42	-4.1112	-3.0270	-3.3142
	44	-3.0652	-2.7025	-2.6651
	47	-2.4633	-2.8770	-3.0141
	50	-2.6872	-3.0558	-3.3718
	53	-3.1445	-2.6613	-2.5827
	55	-2.9759	-2.3700	-2.0002
	58	-2.0441	-2.6491	-2.5584
	61	-1.1600	-2.7567	-2.7735
	66	-1.2908	-2.4340	-2.1281
	72	-2.5517	-2.4946	-2.2494
{B}/{D}(7%)	42	-4.0186	-2.9901	-3.2404
	47	-4.5746	-3.0604	-3.3810
	51	-3.9488	-2.8115	-2.8832
	56	-2.9113	-3.0276	-3.3154
	61	-2.4487	-3.3731	-4.0064
	65	-2.7729	-3.1179	-3.4961
	70	-3.1766	-2.7686	-2.7974
	76	-2.8615	-2.9544	-3.1690
	90	-1.8632	-3.0579	-3.3760
{A}/{C}(20%)	34	-1.0937	-2.6462	-2.5526
	42	-1.4368	-2.4892	-2.2386
	45	-2.8158	-2.8745	-3.0093
	48	-4.1962	-2.9830	-3.2262
	51	-4.5422	-2.7180	-2.6963
	55	-3.7744	-2.8952	-3.0507
	58	-2.7754	-3.3736	-4.0074
	60	-2.4583	-3.3205	-3.9011
	62	-2.8611	-3.0282	-3.3166
	65	-3.1865	-3.2264	-3.7130
	85	-2.7258	-3.4364	-4.1330
{C}/{B}(7%)	35	-1.6887	-3.0538	-3.3677
	47	-1.0608	-2.7335	-2.7272
	50	-1.6140	-2.9705	-3.2011
	55	-3.0800	-3.0423	-3.3448
	58	-4.3426	-2.6702	-2.6006
	60	-4.4763	-2.6704	-2.6011
	62	-3.5936	-3.1327	-3.5255
	65	-1.0608	-2.7335	-3.6625

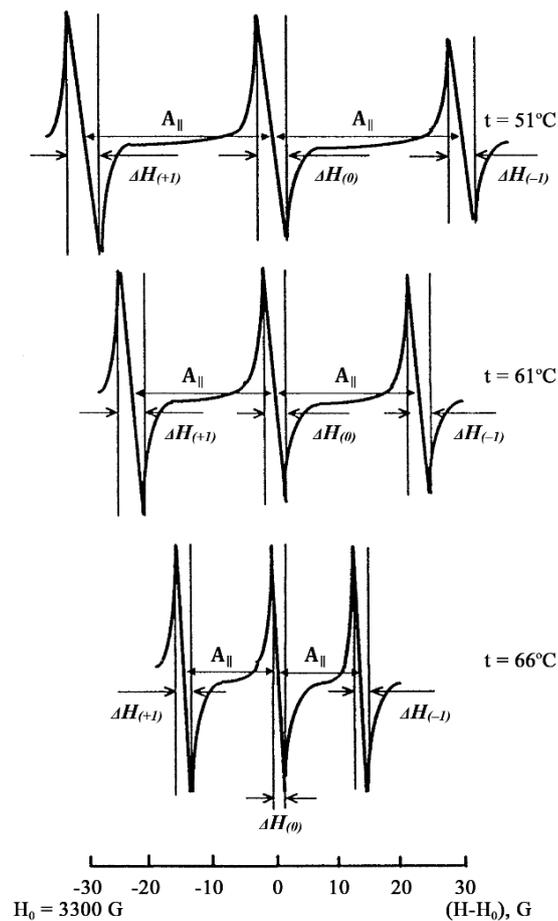
### 3. Discussion of Results and Conclusions

Figure 2 shows the spectra of the nitroxyl radical in the {A}/{C}10% LC system at various temperatures. It is known that the long axis of molecules in the LC phase tend to be oriented parallel to one another. The weighted average orientation of the molecules in the ensemble,

grouped in a relatively small region of the sample, can in this case be characterized by the  $Z$  – direction with respect to which the molecular motion has axial symmetry. In the case of uniformly oriented samples, the simplest situation arises when the  $Z$  – axes in these regions are aligned parallel to each other and all micro regions have the same orientation with respect to the  $\vec{H}_0$  external magnetic field. In nematic LCs, such parallel alignment of the axes is easily caused by the application of a sufficiently strong magnetic field (which is the constant magnetic field used in a conventional ESR experiment). Similarly, smectic phases during slow cooling can also be oriented in a magnetic field. Our quantitative analysis (1) of the shape of the spectra based on the theory of spin relaxation showed that the value of the rotation correlation time  $\tau_c$  of the radical is in the region of fast rotations. In the region of fast rotations ( $10^{-11} < \tau_c < 10^{-9}$  sec) the isotropic reorientation of the spin probe is characterized by a single correlation time  $\tau_r$  which, according to [10], depends on the effective radius  $r$  of the radical, the local viscosity  $\eta$  and the temperature  $T$  of the medium:

$$t_r = 4\pi\eta r^3 / 2kT \tag{2}$$

where  $k$  is the Boltzmann constant.



**Fig.2.** Radical’s spectra in {A}/ {C} 10% LC system at various temperatures.  $\vec{H}_0 \parallel Z$  – axis.

However, if the motion in the LC phase is anisotropic, then the rotation of the radical is not spherically symmetric and cannot be described by a single value.

Under the condition of the fast rotation, the anisotropic rotation of an axially symmetric ellipsoid–radical is characterized by two frequencies:  $\tau_{\parallel}^{-1}$  – corresponds to the rotation of the particle relative to the axis of symmetry; and  $\tau_{\perp}^{-1}$  – corresponds to the rotation of the particle relative to the other axis of the ellipsoid perpendicular to its axis of symmetry. Thus, in order to determine the value of  $\tau_r$ , it is necessary to determine, firstly, both times:  $\tau_{\parallel}, \tau_{\perp}$  and secondly, the distribution of the coordinate axes of the radical fragment  $X', Y', Z'$  with respect to the laboratory coordinate system  $(X, Y, Z)$  (see Table 1).  $\tau_{\parallel}$  and  $\tau_{\perp}$  were found using (1). As our calculations show, in all investigated LC systems the rotation anisotropy parameter  $N = \tau_{\perp}/\tau_{\parallel}$  is temperature independent and equals  $N = 2.1 \pm 0.4$ . The fact of  $N$  constancy corresponds to the rotation hydrodynamic model, which makes the use of expression (2) for estimating the viscosity coefficient  $\eta$  quite justified. And the fact that  $Y'$ – axis of the molecular coordinate system becomes parallel to the  $Z$ – axis of the laboratory coordinate system (Table 1) allows to characterize the radical rotation in the samples with one time:  $\tau_r \approx \tau_{\perp}$ .

**Table 2.** Viscosity characteristics of LC systems in Sm C\* phase ( $t = 52^{\circ}\text{C}$ ).

LC system, mol%	Correlation time $\tau_r, 10^{-10} \text{ sec}$	Viscosity $\eta, (\text{poise}), 10^{-2} P$
{A}/{D}7%	31,3	1,4
{A}/{D}20%	62,4	2,8
{A}/{C}7%	22,4	1,0
{A}/{C}20%	56,5	2,5
{B}/{D}7%	6,2	0,3
{B}/{D}20%	22,7	1,0
{B}/{C}7%	7,4	0,3
{B}/{C}20%	23,5	1,1

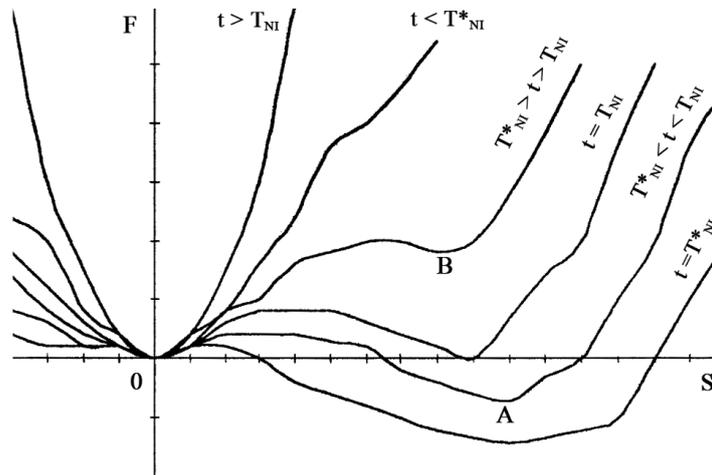
As shown in table 2, an increase in the concentration of additives {C} and {D} in all systems leads to an increase in the viscosity of the medium. In principle, these systems can be considered as an equilibrium mixture of monomers and dimers. Properties of such mixtures depend on the degree of association and the shape of the dimers. Arguments in favor of such a distribution are given in [15, 16]. In [15] the special attention has been paid to the presence of the several deep local extrema on the curve of the  $U_{\text{pair}}$  dependence on displacement along  $X$ –axis, which reflects the conception about the distribution of “active” centers of interaction along a molecule. The existence of these potential barriers, apparently, will be considered as one of the main reasons of local ordering in Sm phase [15]. Mixed dimer molecular agglomerates, being a strong cluster of molecules, are possibly formed (which is due to the presence of  $\text{COO}, \text{OH}, \text{CH}_3$  polar groups, i.e. the structural features of the molecules of the LC system components) in the presence of these potential barriers in the LC systems under consideration. It is reasonable to assume that the

increase in an amount of mixed dimers with an increase in the concentration of additives in LC systems leads to an increase in the viscosity of media. A comparison of  $\eta$  values in systems with the same matrix but with different additives at the same concentration shows that in {A}/{D} (7,20%) LC system the viscosity is higher than in media of {A}/{C} (7,20%) (Table 2). It is assumed that in the investigated polar LC systems the increase in concentration of additives increases the intermolecular interaction, which leads to molecular associates and affects packaging.

Let us consider the nature of phase transitions between a LC mesophase and an isotropic liquid, as well as between different mesophases. These issues are closely related to the nature of mesophases, since subtle physical processes in a very narrow temperature range, where future mesophase begins, predetermine the properties of the mesophase.

Based on the dependence of the LC free energy density ( $F(S)$ ) on the order parameter ( $S$ ) (Fig.3 [17], we can distinguish the following cases:

- at  $t > T_{NI}$  there is one minimum:  $F_{\min}(S) = F(S = 0)$ . It means that only the isotropic phase is stable;
- at  $t = T_{NI}$  there are two minimums:  $F_{1\min}(S) = F(S = 0)$ ,  $F_{2\min}(S) = F(S \neq 0)$
- at  $t = T_{NI}^* < T_{NI}$  there is one minimum:  $F_{\min}(S) = F(S \neq 0)$
- at  $T_{NI} > t > T_{NI}^*$  there are two minimums:  $F_{1\min}(S) = F(S = 0)$ ,  $F_{2\min}(S) = F(S \neq 0)$
- at  $T_{NI} < t < T_{NI}^*$  there are two minimums:  $F_{1\min}(S) = F(S = 0)$ ,  $F_{2\min}(S) = F(S \neq 0)$  ;  $F(S = 0) < F(S \neq 0) \Rightarrow$  nematic phase is metastable.



**Fig. 3.** A schematic representation of the dependence of the density of free energy  $F$  on the order parameter  $S_N$  in nematic LC.

Our multiple microscopic observations and ESR study showed that upon cooling in {A}/{C} and {A}/{D} LC systems IL phase passes into the  $N^*LC$  mesophase at a temperature  $3^0C$

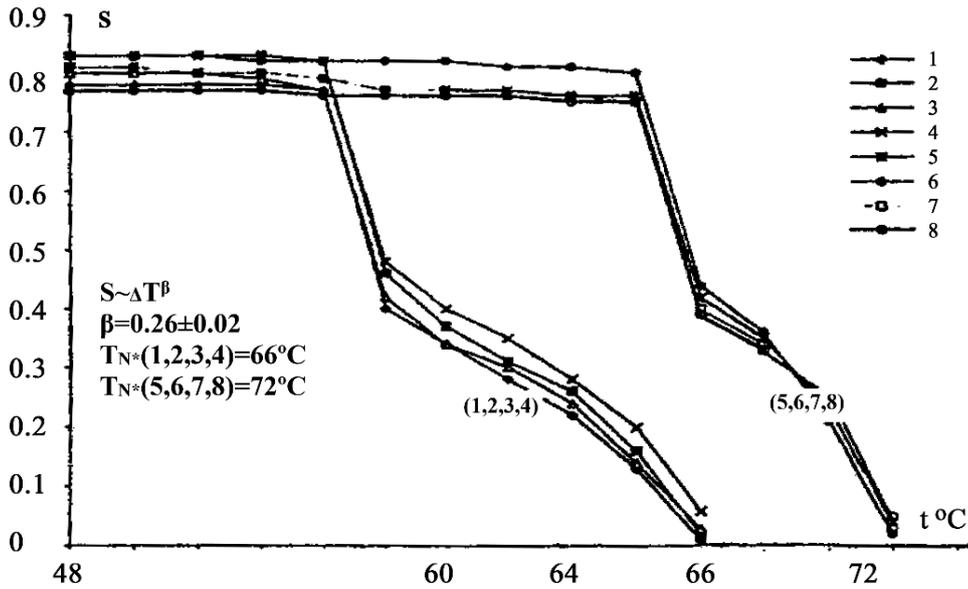
below the temperature at which the reverse transition ( $N^*LC \rightarrow IL$ ) occurs upon heating. In  $\{B\}/\{C\}$  and  $\{B\}/\{D\}$  systems  $IL \rightarrow N^*LC$  phase transition occurs at a temperature  $2^\circ C$  below the temperature of  $N^*LC \rightarrow IL$  phase transition. I.e. in the systems under study, hysteresis takes place. For the Sm A  $LC \rightarrow N^*LC$  phase transition, we note that as in the case of the  $N^*LC \rightarrow IL$  transition, the hysteresis also was observed in the studied systems. It seems that these phase transitions can be classified as first-order phase transitions. However, taking into account a long-range order in the orientation of molecules in  $N^*LC$  mesophase, it turns out that there must be a connection between the nematic and smectic order parameters. This additional condition leads to the fact that, depending on the quantitative criteria [18] related to the classified order of phase transition, the SmA  $LC \rightarrow N^*LC$  transition can be either of the first or second-order. A second-order phase transition is possible if  $\frac{T_{SmAN}}{T_{NI}} < 0.87$ ; and a first-order transition is possible in the case, when  $\frac{T_{SmAN}}{T_{NI}} > 0.87$ .

The order parameter  $S$  was calculated by the following expression [10]:

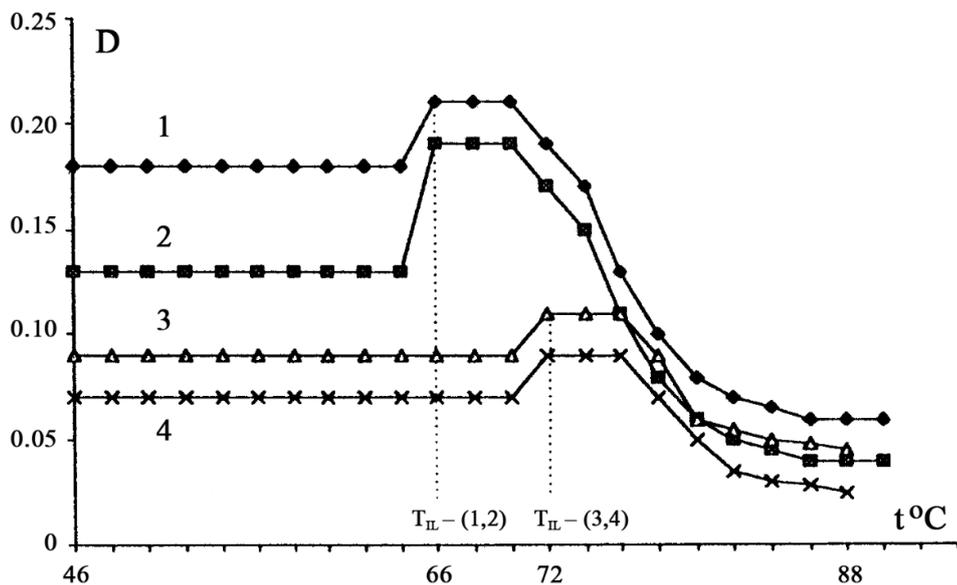
$$S = \frac{A_{\parallel} - A_{\perp}}{A_{z'z'} - A_{x'x'}} \frac{a_N}{a'_N} \quad (3)$$

where  $a_N = \frac{1}{3}(A_{x'x'} + A_{y'y'} + A_{z'z'})$  is the isotropic hyperfine splitting constant;  $a'_N$  is defined by the expression  $a'_N = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$  that is equivalent to the expression for  $a_N$ . However, “'” indicates that the polarity values are not identical in the single crystal and the LC phase and  $a'_N$  as a correction is introduced into expression (3).

Calculation results of  $S$  as a function of temperature are given in Fig. 4. Consider the  $N^*LC \rightarrow IL$  phase transition. Aforementioned existence of thermal hysteresis (typical for the first-order phase transitions) in systems under study, predicts an intermittent behavior of  $S$ . However, as can be seen from Fig.4, at the  $N^*LC \rightarrow IL$  phase transition,  $S$  does not decrease abruptly. The requirement of an intermittent behavior of  $S$  follows from the consideration of this transition in the framework of Landau's theory of phase transitions [9]. This is because in Landau's theory assumed that  $S$  does not depend on spatial coordinates. In fact, in the vicinity of  $N^*LC \rightarrow IL$  phase transition (directly above the  $T_{N^*I}$ ), in the isotropic phase, the regions, in which the molecules have a nematic order (cybotactic groups) are observed. The existence of these groups was indicated by measurements of the optical density  $D$  as a function of temperature (Fig. 5).



**Fig. 4.** Temperature dependence of the order parameter  $S$  in LC systems:  
 1- $\{A\}/\{D\}$ 7%; 2- $\{A\}/\{C\}$ 7%; 3- $\{A\}/\{D\}$ 20%; 4- $\{A\}/\{C\}$ 20%;  
 5- $\{B\}/\{D\}$ 7%; 6- $\{B\}/\{C\}$ 7%; 7- $\{B\}/\{D\}$ 20%; 8- $\{B\}/\{C\}$ 20%.  
 $T_N^*$ :  $-IL \rightarrow N^*$  transition point upon cooling.  $\Delta T = t - T_N^*$ .



**Fig. 5.** Temperature dependence of optical density  $D$  in LC systems:  
 1-  $\{A\}/\{D\}$ 7%; 2-  $\{A\}/\{C\}$ 7%; 3-  $\{B\}/\{D\}$ 20%; 4-  $\{B\}/\{C\}$ 20%.  
 The direction of the laser beam is parallel to the direction of the  
 planar orientation of the LC cell with a thickness of 20  $\mu\text{m}$ .

On the other hand, the temperature range of Landau's theory applicability is related to molecular parameters by the ratio:

$$\frac{(T - T_{aNI})}{T_{NI}} \geq \frac{\langle r \rangle^6}{r_0^6} \quad (4)$$

where the average distance between molecules is  $\langle r \rangle$  and  $r_0$  is the radius of the intermolecular forces action. If assume that in our LC systems for the ordering of molecules near  $N^*LC \rightarrow IL$  transition the short-range dispersion forces ( $r_0 \approx r$ ) are responsible, then it becomes clear (from condition (4)) why the Landau's theory is not applicable in a significant range of the phase transition temperatures. In the temperature range, where the Landau's theory is not applicable, works well the so-called similarity theory (or scaling theory). According to this theory, the behavior of thermodynamic quantities is entirely determined by the order of correlation radius of cybotactic groups (fluctuation' interaction) and exponentially depend on proximity to the phase transition point. In particular, for the order parameter  $S$  we have [17, 19]:

$$S \sim \Delta T^\beta \quad (5)$$

where  $\Delta T = t - T_{NI}^*$ ,  $\beta$  – is the critical index. In the similarity theory, as well as in Landau's theory of phase transitions, the type of transition can be determined from the value of critical index. Using the results for, calculated with the help of (3), and taken into account (5) for investigated LC systems the critical index  $\beta \approx 0.26$  was obtained.

Based on the obtained experimental and calculated data, as well as from the above conducted theoretical analysis, we can conclude that in studied LC systems the  $N^*LC \rightarrow IL$  phase transition is apparently best described as a combined phase transition, close to the Lifshitz' tricritical point, in the systems with short-range interactions of molecules.

Now discuss the  $SmALC \rightarrow N^*LC$  phase transition. As can be seen from Fig.4, in all LC systems at the  $SmALC \rightarrow N^*LC$  phase transition the value of  $S$  abruptly decreases at  $60^\circ C$  and  $66^\circ C$  for  $\{A\}/\{C\}$ ,  $\{A\}/\{D\}$  and  $\{B\}/\{C\}$ ,  $\{B\}/\{D\}$  respectively. We note that in the McMillan microscopic theory [18] quantitative criteria regarding the  $SmALC \rightarrow N^*LC$  phase transition order were obtained in the dependence of the  $SmALC \rightarrow N^*LC$  phase transition on the proximity of the  $N^*LC \rightarrow IL$  phase transition [17,18, Fig. 3]. In the considered  $\{A\}/\{C\}$ ,

$\{A\}/\{D\}$  and  $\{B\}/\{C\}$ ,  $\{B\}/\{D\}$  LC systems  $\frac{T_{SmAN}}{T_{NI}} = 0.92 > 0.87$  and  $\frac{T_{SmAN}}{T_{NI}} = 0.91 > 0.87$

accordingly. It follows then, that the  $SmALC \rightarrow N^*LC$  phase transition in LC systems under study should have the features of a first-order phase transition, which is in full agreement with the  $S$  behavior (Fig. 4) typical the  $SmALC \rightarrow N^*LC$  first-order transitions. As a result of the study of molecular mobility and ordering in nematic, smectic and ferroelectric LC systems has been shown that the influence of the temperature and structural features of the compound's molecules of LC system on the EPR spectra is due to the presence of smectic fluctuation regions

in the nematic phase, a change in polarity, and complexation in the LC system depending on its composition.

### **Conflict of Interest**

There is no conflict of interest.

### **Author Contributions**

Author L.S. Bezhanova invented and developed the experiment, carried out theoretical calculations. Participated in data processing, participated in the writing of the text.

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