

Characteristics of the behavior of elastic constants of liquid crystals due to reentrant polymorphism

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A study was made of a mixture of 4-hexyloxy-4'-cyanobiphenyl (6OCB) and 4-octyloxy-4'-cyanobiphenyl (8OCB) liquid crystals exhibiting reentrant polymorphism, manifested by a second appearance of the nematic phase as a result of cooling of the smectic *A* phase. The methods of scattering of x rays by fluctuations of the translational order parameter ψ and the scattering of light by fluctuations of the director \mathbf{n} were used to determine the temperature and composition dependences of the longitudinal correlation length ξ_{\parallel} and of the elastic constant K_{33} of the nematic (*N*) and reentrant-nematic (*RN*) phases. It was found that anomalies of the physical properties of liquid crystals dependent on ξ_{\parallel} were governed by the nature of the line representing the smectic *A*–nematic phase transitions and by the position of the reentrant point on this line. The nature of the universal functions describing both the temperature and the composition dependences of the elastic coefficient K_{33} was determined. It was found that the critical part of the elastic coefficient K_{33}^s due to the smectic fluctuations was proportional not only to the correlation length ξ_{\parallel} , but also to the square of the nematic order parameter S . Near the nematic–isotropic liquid phase transition the contribution of the smectic fluctuations to the coefficient K_{33} had a finite value comparable with K_{33} itself.

1. INTRODUCTION

The phase transition from the nematic (*N*) to the smectic *A* phase involves the appearance of a one-dimensional translational order in a three-dimensional liquid. The parameter of the $A \leftrightarrow N$ phase transition is a two-component quantity ψ representing the amplitude and phase of a density wave in the *A* phase:

$$\rho = \rho_0 + \delta\rho, \quad \delta\rho = \text{Re}[\psi \exp(iq_0 z)],$$

where $q_0 = 2\pi/d$; d is the period of the layer structure; the z axis is parallel to the orientation of the director \mathbf{n} . In the nematic phase near the $A \leftrightarrow N$ transition some of physical quantities (elastic constants K_{33} and K_{22} , viscosity γ_1) exhibit anomalous behavior. Moreover, singularities are found in the intensity of the scattering of x rays in the vicinity of the wave vector q_0 of the layer structure. These phenomena are all due to the same physical factor, the increase in the role of fluctuations of the smectic order parameter on approach to the phase transition point T_c (Refs. 1 and 2). For example, the elastic constant $K_{33} = K_{33}^n + K_{33}^s$ contains not only the nematic term K_{33}^n but also a term due to the smectic fluctuations $K_{33}^s \propto \xi_{\parallel}$, where ξ_{\parallel} is the longitudinal correlation length representing a characteristic distance in a nematic in a direction parallel to \mathbf{n} , in which the amplitude and phase of the parameter ψ are correlated:

$$\xi_{\parallel} \propto \tau^{-\nu_{\parallel}}, \quad \tau = (T - T_c)/T_c, \quad K_{33}^s \propto S^2,$$

where ν_{\parallel} is the critical exponent for ξ_{\parallel} and S is the orientational order parameter.³ The intensity of the scattered x rays $I(\mathbf{q})$ in the *N* phase is proportional to the correlation function of the smectic fluctuations $\langle \psi^2(\mathbf{q}) \rangle$, which depends

both on ξ_{\parallel} and ξ_{\perp} (ξ_{\perp} is the correlation radius at right-angles to \mathbf{n} ; \mathbf{q} is the scattering wave vector).

For the universality class $D = 3$, $n = 2$, corresponding to the symmetry (n) and the spatial dimensions (D) of the smectic *A*, we find that $\nu_{\parallel} = \nu_{\perp} = 0.66$ follows from the isotropic scaling approximation.^{1,2} Nevertheless, in most cases there are deviations from such universal behavior and they are due to both the anisotropy of the system ($\nu_{\parallel} \neq \nu_{\perp}$) and due to the interactions between the orientational (S) and translational (ψ) order parameters of a liquid crystal, giving rise to singularities in the phase diagram of a liquid crystal (for example, a reentrant or a tricritical singularity). The existence of singularities in the phase diagram of a liquid crystal has the effect that not all the thermodynamic paths of approach to the phase transition point are equivalent.⁴ The position of a singularity in the phase diagram and the actual form of the phase transition line determine the nature of changes in the properties of the system that depend on ξ well inside the *N*-phase region. Therefore, it would be particularly interesting to study systems exhibiting what is known as the reentrant and nematic polymorphism.⁵ We shall report an investigation of a mixture of 4-hexyloxy-4'-cyanobiphenyl (6OCB) and 4-octyloxy-4'-cyanobiphenyl (8OCB). In the range $x_{6OCB} < 28$ wt.% [$y = x_{6OCB}$ (mol.%) / x_{8OCB} (mol.%) $< y_0 = 0.4267$] these mixtures exhibited the following sequence of phases: isotropic (*I*), nematic (*N*), smectic (*A*), reentrant nematic (*RN*), and crystalline. The phase diagram of the 8OCB-6OCB system plotted using the coordinates T and y is shown in Fig. 1 and it includes a reentrant point (*R*) and a line representing the $A \leftrightarrow N$ phase transitions which can be approximated well by a parabola.⁶ Variation of the composition of the system makes it possible to

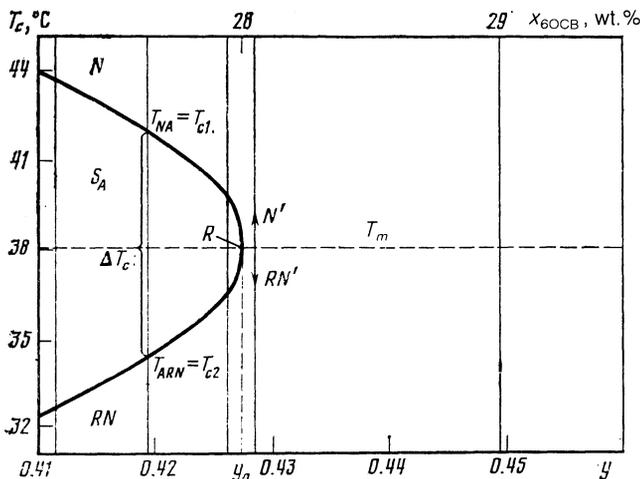


FIG. 1. Phase diagram of mixtures of 6OCB and 8OCB near the reentrant point R . The vertical lines are the composition sections of the diagram.

prepare liquid crystals with different ranges of existence of the N phase and different positions of the composition sections relative to the reentrant point. Allowing for the specific nature of the $A \leftrightarrow N$ phase transition line, the temperature and composition dependences of the correlation length ξ_{\parallel} for 8OCB-6OCB mixtures can be described by the following expressions in the composition ranges $y < y_0$ and $y > y_0$:

$$\xi_{\parallel} = c_{\parallel} [(T - T_m)^2 + \alpha(y - y_0)]^{-\nu_{\parallel}}, \quad y > y_0, \quad (1)$$

$$\xi_{\parallel} = c_{\parallel} [(T - T_{c1})(T - T_{c2})]^{-\nu_{\parallel}}, \quad y \leq y_0, \quad (2)$$

where T_m is the temperature at which ξ_{\parallel} is maximal; α is a parameter governed by the dependence of the critical temperature on the composition and density; c_{\parallel} is a constant; T_{c1} and T_{c2} are the temperatures on the $N \leftrightarrow A$ and $RN \leftrightarrow A$ transitions.

The x-ray scattering method makes it possible to determine directly the correlation length ξ_{\parallel} of the nematic phase. A determination of the intensity of the scattering of light by fluctuations of the director in the N and RN phases makes it possible to find the elastic constants of liquid crystals. Our aim was to establish a correlation between the values of ξ_{\parallel} and K_{33} in the N and RN phases, to determine the influence of the $A \leftrightarrow N$ phase transition line on the behavior of the elastic constant K_{33} , to find the function describing the temperature and composition dependences of K_{33} throughout the ranges of existence of the N and RN phases, and to determine the contribution of the smectic fluctuations to K_{33} compared with the regular part throughout the range of existence of the N phase right up to the bleaching temperature T_{NI} .

2. EXPERIMENTAL METHOD

The scattering of x rays by 8OCB-6OCB mixtures of liquid crystals was investigated employing an ADP-1 automatic x-ray diffractometer and a detector sensitive to the linear position.⁷ The spatial resolution of this detector was 0.2 mm. The size of the sensitive surface of the detector was sufficient to record the diffraction pattern in the angular range $0-4^\circ$ with a resolution of 0.01° . Liquid crystals were

oriented in two ways: in a magnetic field of $H \approx 0.2$ T intensity using miniature magnets made of the SmCo_5 alloy or employing an alternating electric field of $E \approx 1$ kV/cm intensity. We used a thermally stabilized chamber in which a crystal could be set in the reflecting position. The temperature in this chamber could be controlled to within 0.02 K and measured with a calibrated thermistor to within 0.01 K.

The intensity of the x rays scattered by a periodic structure in the N , A , and RN phases was related directly to the translational order parameter ψ of the A phase and by its fluctuations in the N phase; according to Ref. 6, we should have

$$\langle \psi^2(\mathbf{q}) \rangle = k_B T \chi / [1 + \xi_{\parallel}^2 (q_{\parallel} - q_0)^2 + \xi_{\perp}^2 q_{\perp}^2], \quad (3)$$

where χ is the generalized susceptibility.

We determined the temperature dependence of the intensity of the scattered x rays along the q_{\parallel} direction ($q_{\perp} = 0$). According to Eq. (3), an analysis of the experimental profiles of the intensity of the scattering in the N phase at various temperatures, carried out allowing for the nature of the phase transition lines described by Eqs. (1) and (2), should make it possible to find the temperature dependence of the correlation length ξ_{\parallel} . On approach to the phase transition point from the N -phase side the intensity of the scattering increased and the angular width of the scattering peaks $\Delta(2\theta)$ decreased, corresponding to an increase in the correlation radius of the smectic fluctuations in the N phase: $\xi_{\parallel} \propto \lambda / \Delta(2\theta)$. The phase transition point T_c could be determined from Fig. 2 to within 0.1 $^\circ\text{C}$ using the characteristic kink in the temperature dependence of $\Delta(2\theta)$. In the A phase the angular width of the scattered-intensity profile was practically constant, since it became of the same order of magnitude as the broadening due to the instrumental function.

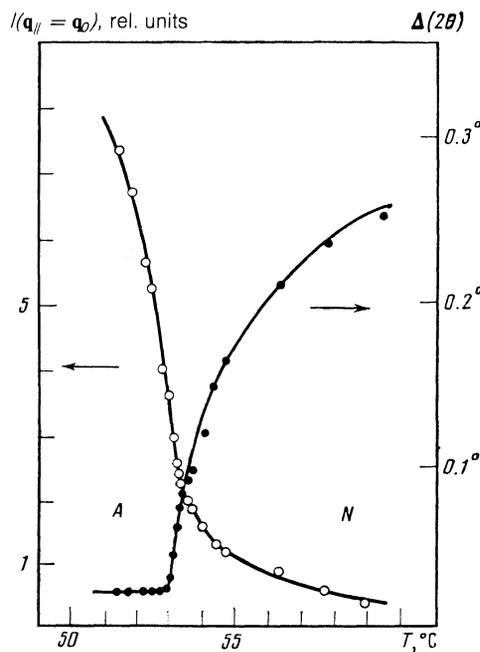


FIG. 2. Angular width of the scattering peaks $\Delta(2\theta)$ and the intensity of the scattered x rays $I(q = q_0)$ obtained for the N and A phases; $y = 0.3$.

TABLE I

$y-y_0$	$\Delta T_c, ^\circ\text{C}$	ν_{\parallel}	Phase	No. of samples	Designation in Fig. 4
-0.4272	59	0.77	<i>N</i>	1	
-0.016	11.2±0.3	0.76±0.005	<i>N</i>	3	○
-0.016	11.2±0.3	0.775±0.003	<i>RN</i>	3	+
-0.008	7.7±0.2	0.76±0.01	<i>N, RN</i>	3	●
-0.0012	3.2	0.761	<i>N</i>	1	□
-0.0012	3.2	0.756	<i>RN</i>	1	□
0.001	—	0.756	<i>N'*</i>	1	▼
0.001	—	0.761	<i>RN'*</i>	1	▼

Note. *The symbols *N'* and *RN'* denote the high- and low-temperature (relative to T_m) regions of existence of the *N* phase.

In the *A* phase, when a regular periodic structure appeared along the *z* axis ($\langle\psi\rangle \neq 0$) the scattering of x rays in samples of finite dimensions was governed by the contributions of the coherent (quasi-Bragg) and noncoherent (fluctuation) scattering:

$$I(\mathbf{q}) = |\psi|^2 \delta(\mathbf{q} - \mathbf{q}_0) + \langle \psi^2(\mathbf{q}) \rangle. \quad (4)$$

The ratio of these contributions was not a universal constant but depended on the parameters of the system, on the proximity to T_c , and on the orienting magnetic field.^{8,9} At temperatures not too close to T_c the temperature dependence of $I(\mathbf{q})$ for the *A* phase was governed by the dependence $|\psi|^2(T)$.

The temperature dependences of the elastic constant K_{33} of 8OCB-6OCB mixtures were determined by the method of light scattering.¹⁰⁻¹⁴ We selected the experimental geometry in which the scattering occurred on a *B* fluctuation mode.¹¹ The intensity of the scattered light i_{sc} was then

$$i_{sc} = A(n_e^2 - n_o^2)^2 T / K_{33}, \quad (5)$$

where A is a constant independent of temperature and governed by the parameters of the apparatus¹¹; T is the absolute temperature; n_e and n_o are the extraordinary and ordinary refractive indices: according to Ref. 3, $(n_e^2 - n_o^2) \propto S$. Assuming that $K_{33}^n \propto S^2$, we find from Eq. (5) that

$$K_{33}^s / K_{33}^n = BT / i_{sc} - 1, \quad (6)$$

where B is a constant. To within terms of the order of S^3 , Eq. (6) applies throughout the range of existence of the *N* phase. The scattering angle ($\varphi = 40^\circ$) was kept constant during our measurements. Additional corrections to the scattering cross section due to the temperature dependences of n_e and n_o (Ref. 15) did not exceed 3% throughout the investigated range of temperatures and were therefore ignored. In these experiments we used planar oriented samples of thicknesses 42 and 66 μ . The temperature of a sample was measured to within 0.015 $^\circ\text{C}$. The compositions of the mixtures are listed in Table I (y is the ratio of the molar fractions of 6OCB and 8OCB, and y_0 is the concentration of 6OCB at which $\Delta T_c = 0$). The value of y_0 was 0.4272 for our sample; the corresponding value of y_0 given in Ref. 6 was 0.4267.

The reciprocal of the scattered light intensity i_{sc}^{-1} varied most rapidly in the region of the $N \leftrightarrow A$ and $A \leftrightarrow RN$ transitions but there were no discontinuities on transition from one phase to the other. This was used in an approximate (to

within 0.1–0.15 $^\circ\text{C}$) determination of the phase transition temperatures T_c . More accurate values of T_c were obtained as a result of a statistical analysis of the experimental results. This analysis included the use of data in the temperature range $|T - T_c| > 0.2$ –0.3 $^\circ\text{C}$ where the proportionality between K_{33}^s and ξ_{\parallel} was known to be obeyed ($\xi_{\parallel} q_{\parallel} < 1$ —see Ref. 2).

In a mathematical analysis of the results of measurements we also obtained the values of K_{33}^n (it was assumed that $K_{33}^n \propto S^2$). These values were compared with the elastic constant representing transverse bending K_{11} measured by the method of Ref. 16.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 3 shows the temperature dependences of the density of the meridional reflection $I(\mathbf{q} = \mathbf{q}_0)$ and the ratio of the elastic constants K_{33}/K_{11} obtained for a number of compositions. In all cases the intensity of the scattered x rays varied nonmonotonically as a result of cooling and the maximum intensity occurred at a temperature T_m corresponding to the midpoint of the range of existence of the *A* phase or it corresponded to the continuation of the axial section of the parabola in the *N* phase. The temperature dependence of the intensity for the first meridional reflection of the *A* phase represented, in accordance with Eq. (4), the temperature dependence of the square of the amplitude of a density wave which decreased on approach to the $N \leftrightarrow A$ and $RN \leftrightarrow A$ phase transition points. A similar temperature dependence was observed also for the elastic constant K_{33} in the range $y > y_0$. As in the case of liquid crystals that have the smectic *A* phase but do not exhibit reentrant polymorphism, the investigated mixtures exhibited in the range $y < y_0$ a critical rise of K_{33} on approach to the temperature of the transition to the smectic phase from the *N*- or from the *RN*-phase side.

The temperature dependences of K_{33} for the *N* and *RN* phases, like those for the *N* phase in the $y > y_0$ case, were symmetric relative to the axial section of the parabola $T = T_m$. The qualitative behavior of the quantities K_{33} and $I(\mathbf{q})$ in the range $y > y_0$ was very similar, which was not surprising since the continuation of the axial section of the parabola for the *N* phase corresponded, in accordance with Eq. (2), to the maximum of the correlation length ξ_{\parallel} .

A quantitative analysis of the temperature dependences of K_{33} in the ranges $y > y_0$ and $y < y_0$ was carried out on the basis of Eqs. (1) and (2). The fitting parameters were the

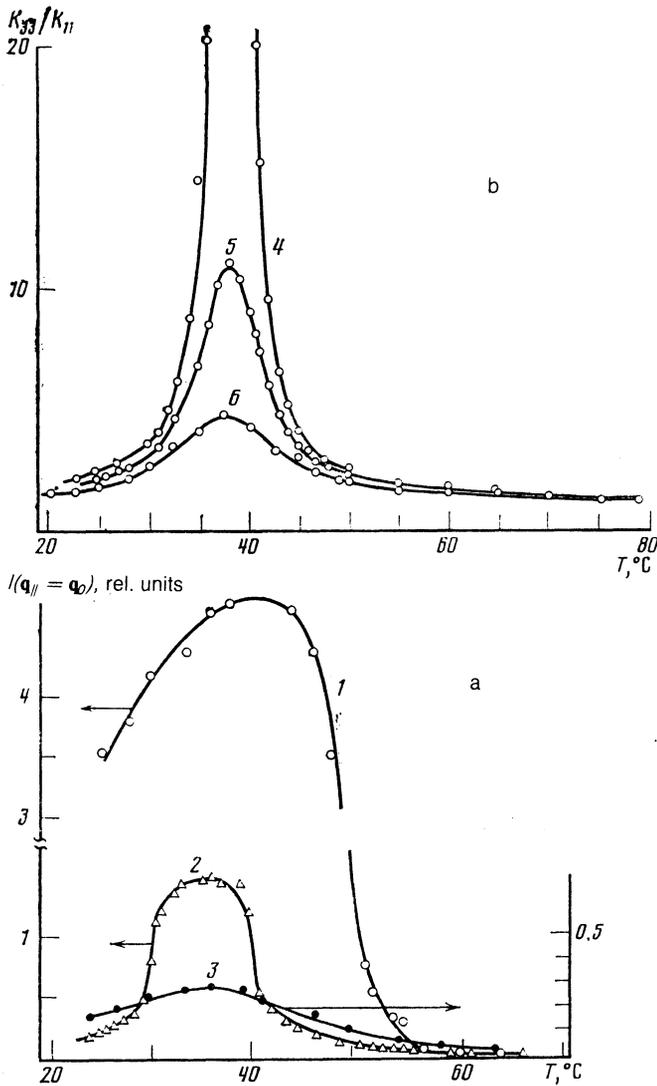


FIG. 3. Temperature dependences of the intensity of the meridional reflection $I(q=q_0)$ (a) and of the ratio of the elastic constants K_{33}/K_{11} (b) obtained for several compositions: 1) $y = 0.3$; 2) $y = 0.413$; 3) $y = 0.43$; 4) $y - y_0 = -0.016$; 5) $y - y_0 = -0.0012$; 6) $y - y_0 = 0.001$.

constant B and the temperatures T_c and T_m , which were selected so that the sum of the squares of the deviations of the values of the ratio K_{33}^s/K_{33}^n calculated using Eq. (6) from those deduced from the measured intensity of the scattered light [Eq. (5)] was minimal. The values of the temperatures T_{NA} and T_{ARN} were varied in the range 0.1–0.2 °C. The difference $\Delta T = T_{NA} - T_{ARN}$ found in this way for all the samples is given in Table I for the N and RN phases. The temperature dependences of K_{33}^s/K_{33}^n of all these samples are plotted in Fig. 4 on a double logarithmic scale. This figure includes also the temperature dependence of the correlation length calculated from the data on the scattering of x rays (Fig. 2) for one of the compositions ($y = 0.3$). The corresponding critical exponent of $\xi_{||}$ was found to be $\nu_{||} = 0.72 \pm 0.06$.

It is clear from the data in Fig. 4 that Eqs. (1) and (2)

provide a universal description of the temperature and composition dependences of the elastic constant K_{33} practically throughout the investigated range of temperatures and compositions from the region in the immediate vicinity of T_c to T_{NI} . The value of the critical exponent $\nu_{||}$ for the N and RN phases is practically constant for all the samples (0.75–0.78). An analysis of the results obtained in the temperature range 55–75 °C gives a somewhat smaller value $\nu_{||} = 0.73 \pm 0.01$, which nevertheless differs from the average.

We thus find that the temperature dependences of K_{33}^s/K_{33}^n and $\xi_{||}$ coincide throughout the investigated range of existence of the N phase right up to T_{NI} . Since $K_{33}^n \propto S^2$, it follows that the temperature dependence of K_{33}^s is of the form $K_{33}^s \propto \xi_{||} S^2$. According to the theoretical ideas,^{1,2} the temperature dependence of K_{33}^s is governed entirely by the temperature dependence of the correlation length. In the case of liquid crystals with a wide range of existence of the N phase near the transition temperature to the A phase this is justified since the dependence $S(T)$ is then weak. If we take the range of temperatures close to T_{c1} and T_{c2} inside which the temperature dependence of S can be ignored, we find that the elastic constant representing longitudinal bending is $K_{33}^s \approx K_{33}^n \propto \xi_{||}$. However, extrapolation of this dependence, which is generally valid near T_{NA} and T_{RNA} , to the range of temperatures close to T_{NI} is not justified because it would give a result in conflict with the experimental data. The dependence $K_{33}^s \propto \xi_{||}$ in the limit $T \rightarrow T_{NI}$ shows that $K_{33}^s \approx K_{33}^n$, i.e., that $K_{33}^s/K_{33}^n \approx K_{33}^s/K_{11} = 2$, since near the temperature T_{NI} we have $K_{33}^n \approx K_{11}$ (Fig. 5). However, a direct determination of the ratio K_{33}/K_{11} near T_{NI} gave 1.15 (Fig. 3). Moreover, the results plotted in Fig. 4 indicated that $K_{33}/K_{33}^n = 1.17$ in the limit $T \rightarrow T_{NI}$. Therefore, the temperature dependence of K_{33} could be described throughout the range of existence of the N phase if an allowance was made for the dependence of K_{33}^s on the nematic order parameter. This clearly implies the need to review the existing phenomenological descriptions of the $N \leftrightarrow A \leftrightarrow RN$ phase transitions, from which we cannot deduce in any way the proportionality of K_{33}^s to ξ and S^2 .

It follows from the results of Ref. 17 that the critical exponent $\nu_{||}$, determined from the light scattering results (it is assumed that $K_{33} \propto \xi_{||}$), is systematically greater (by $\approx 5\%$) than the value deduced from the x-ray structure. This discrepancy may be due to the fact that the analysis is carried out in the range of temperatures where we cannot ignore the temperature dependence of S . A similar difference between the critical exponents of $\xi_{||}$ and K_{33} is observed in our case.

In the immediate vicinity of the nematic–isotropic liquid transition we found that all the samples were characterized by $K_{33}/K_{33}^n \approx 1.17$ (Fig. 4). It follows that the contribution of the smectic fluctuations does not disappear at $T \approx T_{NI}$ and it still has a finite value at this temperature. In fact, extrapolation of the dependence $\xi_{||}(T)$ to the temperature range $T \approx T_{NI}$ shows that even far from the phase transition point in the N phase the correlation length is of the order of two or three interlayer periods (Fig. 4). The contribution

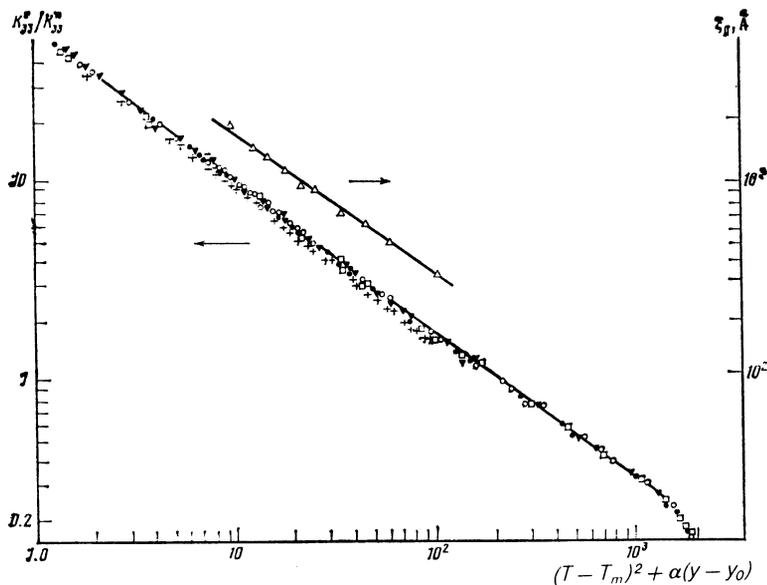


FIG. 4. Temperature dependences of the correlation length ξ_{\parallel} ($y = 0.3$) and of the ratio K_{33}^s / K_{33}^n obtained for several compositions (the compositions are identified in Table I).

of smectic fluctuations to K_{33} near T_{NI} reflects also the difference between the value of K_{33}/K_{11} and unity, since in the case of the majority of nematic liquid crystals we find that $K_{33}/K_{11} \rightarrow 1$ at temperatures $T \rightarrow T_{NI}$ (Ref. 18). In our case at $T \approx T_{NI}$ we find that $K_{33}^n = K_{11}$, if we limit ourselves only to terms of the order of S^2 in the free-energy expansion (Fig. 5). The ratio $K_{33}/K_{11} = 1.15$ has been determined independently by the method of light scattering on a fluctuating S mode.¹¹

4. CONCLUSIONS

1. The investigation reported above demonstrates that the $A \leftrightarrow N$ phase line of 8OCB-6OCB liquid crystal mixtures and the position of the reentrant point on this line govern the nature of the anomalies of the physical properties that depend on the longitudinal correlation length ξ_{\parallel} (for example, K_{33}) throughout the range of existence of the nematic and reentrant nematic phases. The anomalous behavior of the

quantities K_{33} and $I(\mathbf{q})$ may be observed in the N phase also in those cases when the R point is unattainable because of crystallization of the substance or formation of other smectic phases (C , B , etc.). The influence of such singularities is manifested also by a change of the slope of the $A \leftrightarrow N$ phase transition line.

2. In the case of mixtures of 6OCB and 8OCB in the range of compositions corresponding to limit of reentrant polymorphism the ratio of the elastic constants K_{33}^s / K_{33}^n can be described by a universal function of temperature and composition, governed by the nature of the $A \leftrightarrow N$ phase transition line. This means that the critical part of the elastic constant obeys $K_{33}^s \propto \xi_{\parallel} S^2$, where S is the orientational order parameter. The difference between the ratio of the elastic constants K_{33}/K_{11} and unity near the phase transition between the nematic liquid crystal and the isotropic liquid states demonstrates that the contribution of the smectic fluctuations to the value of K_{33} at $T \approx T_{NI}$ is finite and is comparable with the value of K_{33} itself.

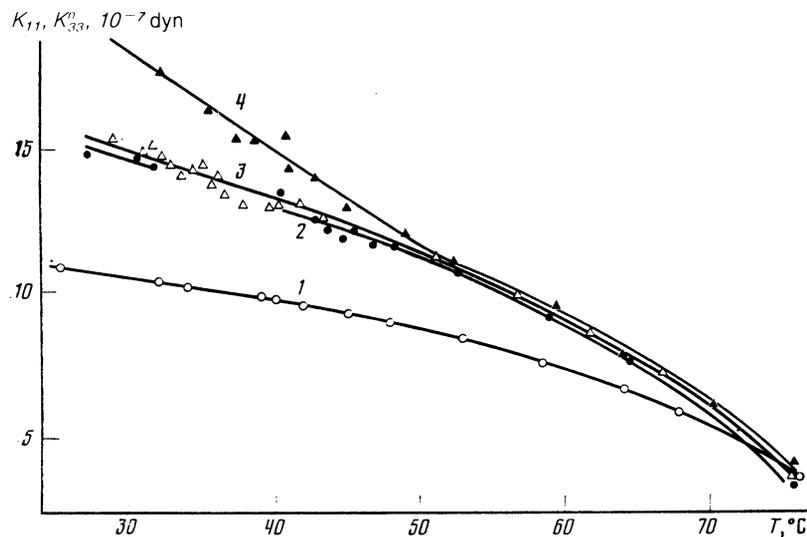


FIG. 5. Temperature dependences of K_{33}^n (curve 1 is calculated from the relationship $K_{33}^n \propto S^2$) and of the elastic constant representing transverse bending K_{11} : 2) $x_{6OCB} = 27.6$ wt.%; 3) $x_{6OCB} = 29$ wt.%; 4) $x_{6OCB} = 30$ wt.%.

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