

Experimental observation of crystallization fluctuations in the isotropic phase of a liquid crystal

V. P. Voronov and F. Kholmurodov¹⁾

Institute of Petroleum and Gas Problems, USSR Academy of Sciences

(Submitted 5 October 1988)

Zh. Eksp. Teor. Fiz. **95**, 1324–1334 (April 1989)

We have measured the heat and the heat capacity on the $I-N$ transition line in mixtures of $\overline{608}$ – $\overline{6010}$ and $\overline{6010}$ – $\overline{6012}$ liquid crystals. We show that the anomalous growth of the $I-N$ transition heat as the INA triple point is approached is due to crystallization fluctuations in the isotropic phase. The contribution of the crystallization fluctuations to the heat-capacity anomaly in the isotropic phase is identified and is found to become comparable, in the vicinity of the INA triple point, with the fluctuating contribution of the nematic order parameter.

INTRODUCTION

Liquid crystals are unique examples of systems in which crystal lattices of lower spatial dimensionality are realized. In particular, the smectic mesophases A and C are systems with one-dimensional crystal lattices. Features of crystallization of lower dimensionality are the “weakness” of the phase transitions from an isotropic liquid and the presence of homogeneous orientational ordering. It is specifically the interaction of the crystal lattice with the orientational ordering which favors crystallization into a lattice of lower dimensionality¹ over crystallization into the three-dimensional body-centered-cubic lattice predicted by a theory² in which no allowance for this interaction is made.

The transition in liquid crystals from an isotropic liquid is accompanied by a latent heat which is lower by at least an order of magnitude than in ordinary crystallization (in this sense the transition is “weak”) and by a strong homogeneous orientational ordering (the jump of the orientational order parameter usually amounts to 0.4–0.5 of the saturation value).

In view of the “weakness” of the crystallization transitions, the parameter $\Delta = (T_i - T^*)/T^*$ indicative of the proximity of the transition temperature to the susceptibility divergence is small (here T_i is the transition temperature and T^* is the limit of the thermodynamic stability of the isotropic phase). One can therefore expect noticeable contributions to the thermodynamic quantities from the fluctuations of the translational order parameter in the isotropic phase, at least near the INA triple point (the point of intersection of the lines of the three first-order phase transitions $I-N$, N -smectic A , and $I-A$).

The existence of fluctuations of this kind is indicated by the experimentally observed^{3,4} increase of the deviation of the variation of the nematic (orientational) susceptibility in the isotropic phase from the Curie–Weiss law when the width of the nematic mesophase (the temperature interval in which the nematic mesophase exists) is decreased. The influence of smectic fluctuations on the behavior of the nematic susceptibility in the isotropic phase prior to the transition was considered in Refs. 5 and 6. Recent experimental data on light scattering^{4,7} agree with the theory.

Smectic fluctuations (translational-order fluctuations) in the isotropic phase, owing to the anomalously large phase space and to their singular temperature dependence, can be investigated by measuring the fluctuating parts of the entropy and of the heat capacity. We propose here a consistent

description (based on detailed heat-capacity and latent-heat measurements of $I-N$ transitions) of phenomena that occur in the isotropic phase prior to transition and which are connected with fluctuations of the translational order.

THEORETICAL ESTIMATES

Proposing only a qualitative treatment of smectic fluctuations in the isotropic phase, we disregard the influence of orientational-order fluctuations.

The spectrum of a uniaxial smectic mode in the vicinity of the characteristic wave vector q_0 of a smectic lattice can be expressed in the form⁸

$$\Delta(q) = \alpha_{sm} [\Delta + \xi_{0\parallel}^2 (q - q_0)^2], \quad (1)$$

where $\Delta = \Delta_0 + \tau$, Δ_0 characterizes the “unrenormalized” (without allowance for fluctuations) width of the nematic mesophase; $\tau = (T - T_{IN}^*)/T_{IN}$, T_{IN}^* is the nematic-susceptibility divergence temperature; $\xi_{0\parallel}$ is the direct-correlation radius of the smectic fluctuations; and α_{sm} is the coefficient of the quadratic term in the expansion of the Landau free energy in powers of the smectic order parameter ψ . It is assumed here that $\xi_{0\parallel}^2 q_0^2 \gg \Delta$, as is the case for all liquids, since $\xi_{0\parallel} q_0 \sim 1$ while $\Delta \ll 1$.

In the one-loop approximation, the reciprocal smectic susceptibility renormalized by its natural fluctuations is given by

$$\bar{\Delta} = \Delta + \frac{\lambda_{sm}}{(2\pi)^3 4! \alpha_{sm}^2} \int \frac{4\pi q_0 dq}{\Delta + \xi_{0\parallel}^2 (q - q_0)^2},$$

where λ_{sm} is the coefficient of ψ^4 in the Landau expansion. The phase space in the isotropic phase is a spherical layer of radius q_0 and width $dq (dq/q_0 \ll 1)$ equivalent to the assumption $\xi_{0\parallel}^2 q_0^2 \gg \Delta$ and is equal to $4\pi q_0^2 dq / (2\pi)^3$. Integration over all of phase space yields the following expression for the reciprocal smectic susceptibility

$$\bar{\Delta} = \Delta + \frac{\lambda_{sm}}{48\pi \alpha_{sm}^2} \frac{q_0^2}{\xi_{0\parallel}} \bar{\Delta}^{-0.5}. \quad (2)$$

It is now easy to obtain the entropy of the smectic fluctuations in the isotropic phase. In units of the universal gas constant R we have

$$\frac{(S_{sm})_I}{R} = \frac{\alpha_{sm}}{(2\pi)^3} \int_{q_0}^{\infty} \frac{4\pi q_0^2 dq}{\bar{\Delta}(q)} = \frac{q_0^2}{4\pi \xi_{0\parallel}} \bar{\Delta}^{-0.5}. \quad (3)$$

Note that the entropy of the natural fluctuations of the ne-

matic (orientational) order parameter, with respect to which the transition takes place, has an entirely different temperature dependence: $(S_N)_I \propto \tilde{\tau}^{0.5}$.

When orientational ordering appears in the nematic mesophase, the phase volume of the smectic fluctuations is strongly suppressed, consists of two circles of radius $\xi_{0L}^{-1} \tilde{\Delta}_N^{0.5}$ on the q_0 sphere, and is equal to $2\pi dq (2\pi)^{-3} \xi_{0L}^{-2} \tilde{\Delta}_N$. The entropy is therefore given here by

$$\frac{(S_{sm})_N}{R} = \frac{\alpha_{sm} \tilde{\Delta}_N}{(2\pi)^2 \xi_{0L}^2} \int_{q_0}^{\infty} \frac{dq}{\tilde{\Delta}_N(q)} = \frac{1}{8\pi \xi_{0L}^2 \xi_{0\parallel}} \tilde{\Delta}_N^{0.5}, \quad (4)$$

where ξ_{0L} and $\xi_{0\parallel}$ are respectively the transverse and longitudinal direct correlation radii of the smectic fluctuations in the nematic mesophase. Assuming $\xi_{0\parallel} \sim q_0^{-1}$ and $\tilde{\Delta} \sim \tilde{\Delta}_N$ we obtain the jump of the smectic-fluctuation entropy in the transition from an isotropic liquid to a nematic:

$$\frac{(\delta S_{sm})_{IN}}{R} = \frac{(S_{sm})_I}{R} - \frac{(S_{sm})_N}{R} = \frac{q_0^2}{4\pi \xi_{0\parallel}} \tilde{\Delta}^{-0.5} \left(1 - \frac{1}{2} \frac{\xi_{0\parallel}^2}{\xi_{0L}^2} \tilde{\Delta} \right). \quad (5)$$

The value of $\tilde{\Delta}$ is determined from the solution of Eq. (2), which reduces, assuming $A \equiv \lambda_{sm} q_0^2 (48\pi \alpha_{sm}^2 \xi_{0\parallel})^{-1}$, $y \equiv \tilde{\Delta}^{0.5} A^{-1/3}$ and $g \equiv \Delta A^{-2/3}$, to the cubic equation

$$y^3 - gy - 1 = 0. \quad (6)$$

The solution of such an equation as a function of the parameter g is shown in Fig. 1. It can be seen that the renormalized reciprocal susceptibility of the smectic fluctuations does not vanish anywhere, i.e., the imagined temperature at which $\tilde{\Delta}^{-1}$ diverges depends on the susceptibility itself.

From (3) we obtain an expression for the contribution of the smectic fluctuations to the heat-capacity anomaly

$$\begin{aligned} \frac{\delta c_{sm}}{R} &= \frac{q_0^2}{8\pi \xi_{0\parallel}} \tilde{\Delta}^{-1.5} \frac{\partial \tilde{\Delta}}{\partial \tau} \\ &= \frac{q_0^2}{8\pi \xi_{0\parallel}} \tilde{\Delta}^{-1.5} \left(1 + \frac{\lambda_{sm} q_0^2}{48\pi \alpha_{sm}^2 \xi_{0\parallel}} \tilde{\Delta}^{-1.5} \right)^{-1}, \end{aligned} \quad (7)$$

where the derivative $\partial \tilde{\Delta} / \partial \tau$ is obtained from (2). Note that in the Ornstein-Zernike approximation the fluctuational anomaly of the heat capacity of nematic fluctuations diverges, $\delta C_N \propto \tilde{\tau}^{-0.5}$, with a critical exponent $\alpha = 0.5$.

The entropy jump of the smectic fluctuations can be

estimated for the $I-N$ transition in the vicinity of the INA triple point, where $\tilde{\Delta} \sim 10^{-3}$. Neglecting the second term in (5) ($\frac{1}{2} \xi_{0\parallel}^2 \xi_{0L}^{-2} \tilde{\Delta} \sim 10^{-2}$) and assuming $\xi_{0\parallel} \sim l/a \sim 5$ (l and a are the longitudinal and transverse dimensions of the molecules) and $q_0 \sim 2\pi \xi_{0\parallel}^{-1}$, we obtain $(\delta S_{sm})_{INA} / R \sim q_0^2 \tilde{\Delta}^{-0.5} / 4\pi \xi_{0\parallel} \sim 1$, i.e., the smectic-fluctuation entropy jump $\delta S_{sm} / R$ in the vicinity of the INA triple point is larger than the entropy jump $\delta S_N / R \sim (\delta Q)^2 \sim 0.2$ connected with the nematic order parameter, and should make the main contribution to the latent heat of the transition.

EXPERIMENT

We have investigated the behavior of the transition heat on the $I-N$ line and the isobaric heat capacity in the isotropic phase for various nematic-mesophase widths. To obtain samples with smooth variation of the nematic-mesophase width we used binary mixtures of liquid crystals of one homological series: $\bar{6}0\bar{8}-\bar{6}0\bar{10}$ and $\bar{6}0\bar{10}-\bar{6}0\bar{12}$. The sequence of the mesophases in the pure substances is such that the phase diagrams of these mixtures (see Fig. 2) contain an INA triple point, a de Gennes point⁹ on the $N-A$ line, and an $N-A$ -smectic C (NAC) multicritical point. The nematic-mesophase width ranges from zero at the INA triple point to 23.6 K in pure $\bar{6}0\bar{8}$. It is interesting to note that $\bar{6}0\bar{12}$ is the limiting homolog for the existence of a nematic mesophase in this series.

The measurements were made with an adiabatic microcalorimeter¹⁰ having an approximate total volume 0.3 cm³. The characteristic time of thermal equalization for a cell of diameter 0.5 cm was less than 5 min. The calorimetry cell was hermetically sealed and placed in a copper vessel with a heater surrounded by two heat screens. The conducting leads were glued beforehand in tandem on two copper blocks. The temperatures of the screens and of the blocks followed automatically the temperature of the calorimetry cell. The temperature-difference sensors were three-junction Chromel-Copel thermocouples of sensitivity $\sim 200 \mu V/K$. The entire assembly was evacuated to $\sim 10^{-4}$ Torr. The total heat exchange of the cell at $T \sim 100^\circ C$ was $\sim 10^{-3}$ W/K. The temperature was measured with a TSPN-5 platinum resistance thermometer placed on the inner heat screen.

The $I-N$ transition heat was determined in an adiabatic-scanning regime from the cell-enthalpy change δH for the $I-N$ transition on the $H(T)$ curve at constant heating power P (see Fig. 3). The heating power could be varied in a wide range. The characteristic heating rate outside the transition region, which we used to measure the heat of the $I-N$ transi-

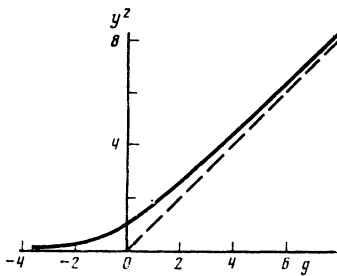


FIG. 1. Dependence of the square of the root of Eq. (6) on the parameter g or, on the $A^{-2/3}$ scale, dependence of the renormalized smectic susceptibility $\tilde{\Delta}$ in the isotropic phase on the parameter $\Delta = \Delta_0 + \tau$ that characterizes the proximity to the "unrenormalized" line of the $N-A$ phase transitions.

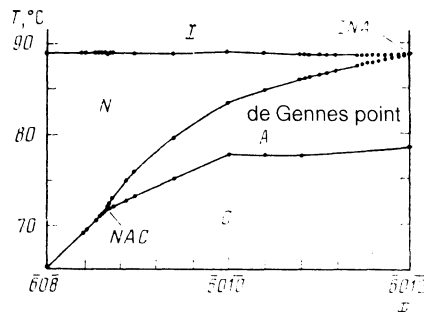


FIG. 2. $T-x$ phase diagram of the mixtures $\bar{6}0\bar{8}-\bar{6}0\bar{10}$ and $\bar{6}0\bar{10}-\bar{6}0\bar{12}$.

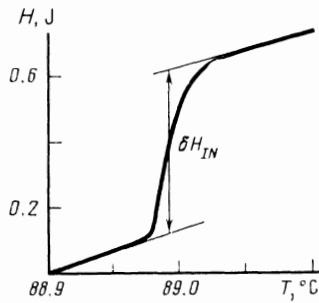


FIG. 3. Typical plot of the enthalpy $H(T)$ in the vicinity of an $I-N$ phase transition for a heating rate $\sim 5 \cdot 10^{-5}$ K/s.

tion, was $\sim 5 \cdot 10^{-5}$ K/s. The transition heat $(\delta H)_{IN}$ was determined by extrapolating $H(T)$ to the midpoint of the transition, to take into account the contribution due to the heat capacity, since the transition takes place in a finite temperature interval ΔT_{IN} . We extrapolated from a region close to the transition ($|T - T_{IN}| \sim 10^{-2}$ K), thereby excluding the contribution to the transition heat from the pre-transition anomaly of the heat capacity. The error of $(\delta H)_{IN}$ was less than 3%.

The heat capacity was measured by stepwise heating the sample, followed by recording the equilibrium temperature of each step. The onset of thermodynamic equilibrium in the sample was monitored by checking the calorimetry-cell linear temperature variation typical of this regime. The temperature rise ΔT (the calorimetric step) was determined by extrapolating to the midpoint of the rise the equilibrium temperature dependences before and after the heating. The adiabatic-regime stability achieved in our calorimeter made it possible to measure, the temperature rise ΔT accurate to $\sim 10^{-4}$ K, using a small sample (the total heat capacity of the calorimetry cell with the sample was ~ 1 J/K). The heat-capacity measurement error depended on the calorimetry step and was $\sim 0.05\%$ far from the transition and $\sim 1\%$ in its immediate vicinity ($T - T_{IN} \lesssim 0.05$ K).

We have paid particular attention to filling the cell with the sample. Each component with a particular concentration was weighed, and the mixture in the cell was outgassed with $T > T_{IN}$. After outgassing the free volume in the cell was filled with dry nitrogen and the cell hermetically sealed. Before it was placed in the calorimeter, the cell with the sample were heated to ~ 10 K above the temperature of the transition to the isotropic state, and thoroughly shaken to make the sample composition uniform in the cell. Next, without letting the sample cool below the crystallization temperature (by preheating the screens), the cell was placed in the calorimeter, and for the rest of the experiment the liquid was no longer cooled before crystallization. The calorimeter construction allowed the entire procedure to be completed in several minutes.

SMECTIC-FLUCTUATION ENTROPY JUMP ON THE $I-N$ PHASE TRANSITION LINE

The measured heats $(\delta H)_{IN}$ of $I-N$ transitions of 44 concentrations of $\bar{6}0\bar{8}$ - $\bar{6}0$ $\bar{1}0$ and $\bar{6}0$ $\bar{1}0$ - $\bar{6}0$ $\bar{1}2$ mixtures are shown in Fig. 4 in dimensionless form ($(\delta H)_{IN}/RT_{IN} \equiv \delta S_{IN}/R$) as functions of a nematic mesophase width $T_{IN} - T_{NA}$ or $T_{IN} - T_{NC}$. At the INA triple point the transition heat has a discontinuity due to the additional contri-

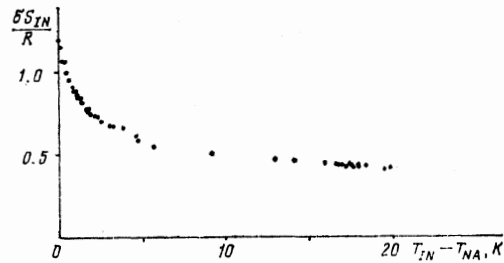


FIG. 4. Entropy jump, in units of R , on the $I-N$ phase transition line as a function of the nematic-mesophase width.

bution from the smectic ordering (the $N-A$ line is a first-order transition line in the vicinity of the triple point). Therefore $(\delta H)_{IN}$ at the triple point was defined as the difference between the total heat $(\delta H)_{INA}$ and the heat on the $N-A$ line,⁹ extrapolated to the triple point. As the nematic-mesophase width decreases the entropy jump on the $I-N$ line increases anomalously. The size of this jump is determined by two contributions, the jump connected with the nematic order parameter (equal to $(\delta S_{IN})_N/R \sim (\delta Q)_{IN}^2$ in the Landau theory) and the jump $(\delta S_{IN})_{sm}/R$ of the smectic fluctuations on the $I-N$ transition:

$$\delta S_{IN}/R = \alpha_N (\delta Q)_{IN}^2 + (\delta S_{IN})_{sm}/R.$$

Direct measurements¹¹ of the nematic order parameter in the $I-N$ line in a 604-406 mixture have shown that the jump δQ_{IN} is practically independent of the nematic-mesophase width. The observed anomalous growth of the entropy jump on the $I-N$ line as the INA triple point is approached is due only to the particular behavior of the smectic fluctuations.

Assuming for the $(\delta S_{IN})_N/R$ contribution the form $(\delta S_{IN})_N/R = B_1 + B_2 \bar{\Delta}$, we have compared the measured $\delta S_{IN}/R$ with Eq. (5). The approximating equation was

$$\delta S_{IN}/R = B_1 + B_2 \bar{\Delta} + B_3 \bar{\Delta}^{-0.5} - B_4 \bar{\Delta}^{0.5} = B_1 + B_2 y^2 + B_3 y^{-1} - B_4 y, \quad (8)$$

where y is the solution of Eq. (6). We have assumed the "unrenormalized" nematic-mesophase width to be a linear function of the concentration x :

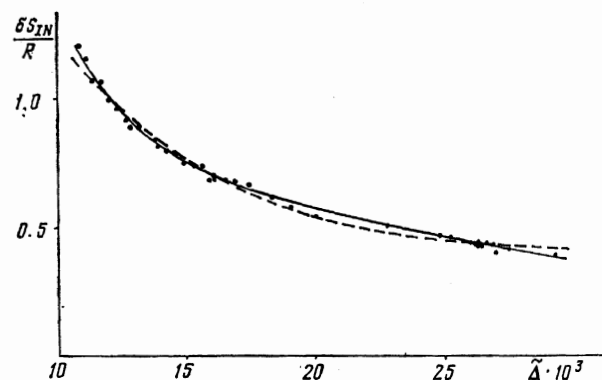


FIG. 5. Entropy jump, in units of R , on the $I-N$ phase transition line as a function of the renormalized smectic susceptibility $\bar{\Delta}$. Solid curve— independent approximation by Eq. (8), dashed—approximation by Eq. (8) with the constants A , A_1 and A_2 obtained from the heat capacity of the smectic fluctuations.

TABLE I. Values of the parameters used to approximate $\delta S_{IN}/R$ by Eq. (8) and δC_{sm} by Eq. (9).

Approximated quantity	A	A ₁	A ₂	B _c	\tilde{B}_2	\tilde{B}_3	\tilde{B}_4
$\frac{\delta S_{IN}}{R}$	$8 \cdot 10^{-5} \pm 5 \cdot 10^{-5}$ ($9.4 \cdot 10^{-5}$)	3.8 ± 0.8 (3.28)	0.22 ± 0.2 (3.42)	— —	— 0.19 ± 0.02	1.22 ± 0.05 5.18 ± 0.22	0.043 ± 0.01 1.0 ± 0.07
$\frac{\delta C_{sm}}{R}$	$9.4 \cdot 10^{-5} \pm 8 \cdot 10^{-5}$	3.28 ± 0.1	3.42 ± 0.9	484 ± 300	—	—	—

Note. The values in the parentheses are the parameters that were not varied in the data reduction.

$$\Delta = T [T_{IN}^* - A_1(2-x) - A_2]^{-1} - 1,$$

with $x = 0$ for $\bar{6}0\bar{8}$ and $x = 2$ for $\bar{6}0\bar{1}2$.

The results of the approximation of $\delta S_{IN}/R$ are shown by the continuous line in Fig. 5 as a function of Δ . All the parameters $A, A_1, A_2, \tilde{B}_2, \tilde{B}_3,$ and \tilde{B}_4 (see Table I) were varied to fit, but B_1 as assumed equal to 0.2. This value accords with the nematic-parameter jump typical of the $I-N$ transition, of order $\delta Q_{IN} = 0.4 - 0.5 (\alpha_N \sim 1)$.

It can be seen from Fig. 5 that the approximation with which Eq. (5) was obtained describes well the experimental data. Moreover, the estimate above of the jump $(\delta S_{IN})_{sm}/R$ for the INA triple point is close to the actual $(\delta S_{INA})_{sm}/R \approx 1$.

An increase of the $I-N$ transition heat with decrease of the nematic-mesophase width in binary liquid-crystal mixtures was observed earlier in Ref. 12. The mechanism of this

phenomenon has not been explained and the growth of the heat of the transitions on the $I-N$ line is attributed to interaction of the orientational and translational order parameters. This explains also the anomalous decrease, observed in Ref. 12, of the heat on the $I-N$ transition line in a concentration region corresponding to the position of the NAC multicritical point. No change of the behavior of $\delta S_{IN}/R$ was observed in our measurements for this region (see Fig. 3). Note that the measurements in Ref. 12 used a differential scanning calorimeter at the usual heating rate of this method, several degrees per minute (three orders larger than our heating rate), so that the true latent heat of the transition cannot be distinguished from the heat due to the pretransition anomaly of the heat-capacity.

CONTRIBUTION OF SMECTIC FLUCTUATIONS TO THE HEAT-CAPACITY ANOMALY OF AN $I-N$ TRANSITION TO THE ISOTROPIC PHASE

Transitions from an isotropic liquid to a liquid-crystal mesophase are of first order close to second, preceded by strongly pronounced fluctuational phenomena. Figure 6 shows the behavior of the isobaric heat capacity in units of R in the vicinity of the $I-N$ transition for the pure components $\bar{6}0\bar{8}, \bar{6}0\bar{1}0,$ and $\bar{6}0\bar{1}2$.

The anomalous (fluctuating) part of the heat capacity in the isotropic phase is made up of the heat capacity $\delta C_N \propto \tau^{-0.5}$ of the nematic fluctuation and the heat capacity

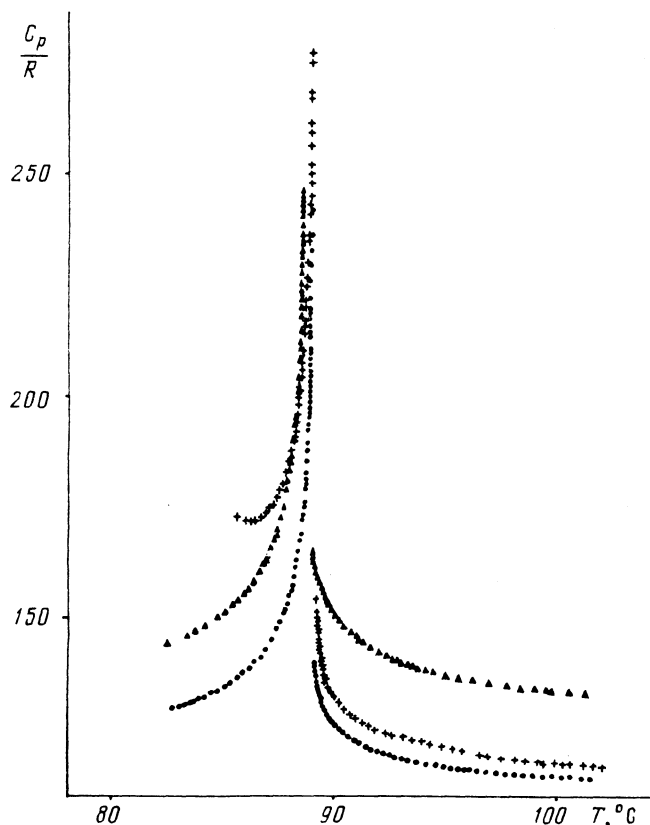


FIG. 6. Behavior of the isobaric heat capacity, in units of R , in the vicinity of an $I-N$ transition in pure components: ●— $\bar{6}0\bar{8}$, +— $\bar{6}0\bar{1}0$, ▲— $\bar{6}0\bar{1}2$.

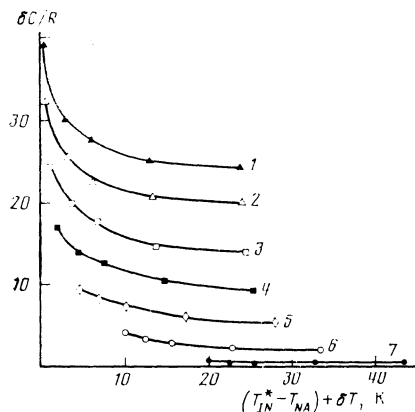


FIG. 7. Anomalous part of the heat capacity in the isotropic phase as a function of the nematic-mesophase width $(T_{IN}^* - T_{NA})$ for various distances δT from the $I-N$ transition: $\delta T = 0.3$ K (curve 1), 0.5 K (2), 1.0 K (3), 2 K (4), 4.5 K (5), 10 K (6), 20 K (7) (the figure shows only several of 16 curves).

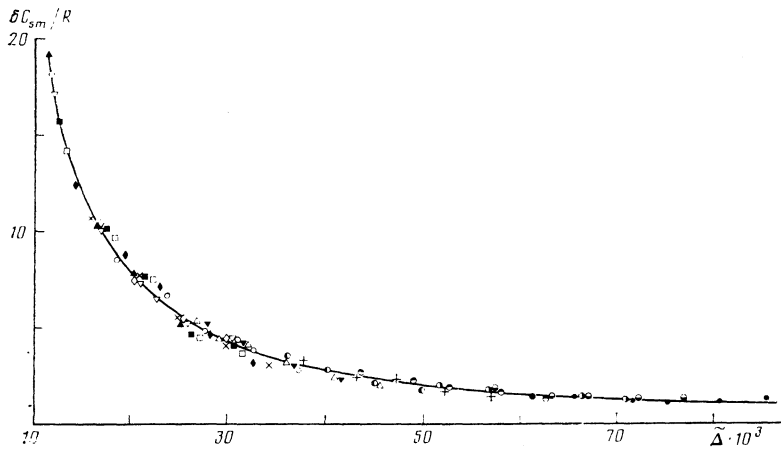


FIG. 8. Universal dependence of the heat capacity of the smectic fluctuations in the isotropic phase on the smectic susceptibility $\tilde{\Delta}$. The different symbols correspond to different δT (see the text): \blacktriangle —0.3 K, \diamond —0.4 K, ∇ —0.5 K, \blacksquare —0.7 K, \square —1 K, \blacklozenge —1.4 K, \times —2 K, \circ —3 K, \blacktriangledown —4.5 K, \triangle —6 K, \bullet —7.5 K, $+$ —10 K, \ominus —12 K, \odot —15 K, \ominus —17 K, \bullet —20 K.

$\delta C_{sm} \propto \tilde{\Delta}^{-1.5}$ of the smectic fluctuations; the latter depends on the nematic-mesophase width. It is practically impossible to distinguish the heat-capacity anomaly components δC_N and δC_{sm} obtained from the experimental temperature dependence of the heat capacity. The smectic-fluctuation contribution is to all appearances the regular part of the heat capacity in the $I-N$ transition (as a rule $\tilde{\Delta} \gg \tau_{IN}$, with $\tilde{\Delta} \sim \tau_{IN}$ only near the triple point). Recognizing, however, that δC_{sm} depends strongly on the width of the nematic mesophase, we can attempt somehow to distinguish between them by using this effect.

In addition to the pure components, we have measured the heat capacities also in the isotropic phases of the mixtures $\bar{60}\bar{8} + 0.481$ mole-fraction of $\bar{60}\bar{10}$ and $\bar{60}\bar{10} + 0.428$ mole-fraction of $\bar{60}\bar{12}$. The nematic-mesophase widths of this set of substances ranged from zero to 23.6 K (see Fig. 2). Far from the $I-N$ transition ($\tau \gtrsim 0.1$) both fluctuating contributions, δC_N and δC_{sm} are negligible and the heat capacity contains only the regular part $C(x)_{reg} \approx C(x, \tau \gtrsim 0.1)$. Figure 7 shows experimental plots, of $\delta C = C(x, T) - C(x)_{reg}$, corresponding to various distances from the transition ($\delta T = \text{const}$), as functions of $T - T_{AN}(x) = T_{IN}^*(x) - T_{AN}(x) + \delta T$. We took $C(x)_{reg}$ to be the heat capacity at $T = T_{IN}^* + 30$ K. Each curve shows the dependence on the nematic-mesophase width $T_{IN}^*(x) - T_{AN}(x)$ only. The temperature T_{IN}^* of the divergence of the nematic susceptibility was determined by an independent reduction of $C(T)/R$ for each concentration.

At temperatures close to those of the $I-N$ transition (curve 1) the anomalous part of the heat capacity for con-

stant δT increases as the nematic-mesophase width decreases, whereas far from the transition (curve 7) it remains practically constant. This behavior is qualitatively obvious. Each curve of Fig. 7 represents the contribution of the smectic fluctuations to the heat-capacity anomaly, a contribution that decreases as the distance from the $I-N$ transition increases. As a first approximation it can be assumed that the magnetic-fluctuation heat capacity $\delta C_N/R$ depends only on the proximity to T_{IN}^* . The $\delta C(\delta T)$ curves are then simply displaced, accurate to a constant, each by an amount equal to the heat capacity $\delta C_N/R$ of the nematic fluctuations, i.e.,

$$\delta C(\delta T = \text{const})/R = \delta C_N/R + \delta C_{sm}/R,$$

and $\delta C_N/R = \text{const}$ if $\delta T = \text{const}$. Consequently, by subtracting $\delta C_N(\delta T)/R$ from $\delta C(\delta T)/R$ we should obtain the contribution of the smectic fluctuations to the heat-capacity anomaly, or, in the $\tilde{\Delta}$ scale, a universal $\delta C_{sm}(\tilde{\Delta})$ curve.

Figure 8 shows $\delta C_{sm}/R$ obtained in this manner as a function of $\tilde{\Delta}$. The solid curve shows the theoretical relation (7) that in the above notation takes the form

$$\delta C_{sm}/R = B_c / (2y^2 + 1), \quad (9)$$

where $B_c = A^{-1} q_0^2 / 4\pi \epsilon_{0||}$. The universal $\delta C_{sm}(\tilde{\Delta})/R$ curve and its approximation by Eq. (8) are mutually consistent. The quantities $\delta C_N(\delta T)/R$, and also A , A_1 , and A_2 (which are contained in Δ) and B_c are all fitting parameters (see Table I). It can be seen that the obtained $\delta C_{sm}/R$ agree well with the theoretical prediction in the entire range of $\tilde{\Delta}$.

The nematic-fluctuation heat capacity $\delta C_N(\delta T)/R$ obtained accurate to the regular part in the course of separation of the smectic-fluctuation heat capacitance is shown in Fig. 9. Approximation of $\delta C_N/R$ by the relation

$$\delta C_N/R = A_0 \tau^{-\alpha} + B + C\tau$$

yields an effective critical exponent $\alpha = 0.41 + 0.07$. Table II lists the effective values of α obtained from the total heat capacities of the isotropic phases of the investigated substances and from the heat capacities after subtracting the contributions of the smectic fluctuations. Allowance for the heat capacity of the smectic fluctuations alters noticeably the exponent α , which is on the average close to the effective $\alpha = 0.41$.

Note that in the vicinity of the INA triple point the contributions $\delta C_N/R$ and $\delta C_{sm}/R$ are comparable. But even if

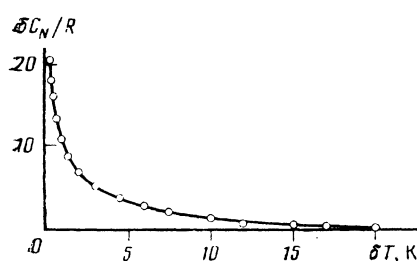


FIG. 9. Heat capacity of the nematic fluctuations as a function of the proximity to the $I-N$ transition; $\delta T = T - T_{IN}^*$ (the curve approximates a power law with exponent $\alpha = 0.41$).

TABLE II. Effective values of the heat-capacity exponent.

Substance	$\bar{608}$	$\bar{608}+0.481$ mole-fraction 6010	$\bar{6010}$	$\bar{6010}+0.428$ mole-fraction 6012	$\bar{6012}$
α { total heat capacity with the contribution $\delta C_{sm}/R$ subtracted	0.26±0.02	0.24±0.02	0.11±0.02	0.2±0.07	0.18±0.04
	0.37±0.02	0.40±0.02	0.30±0.02	0.42±0.05	0.43±0.05

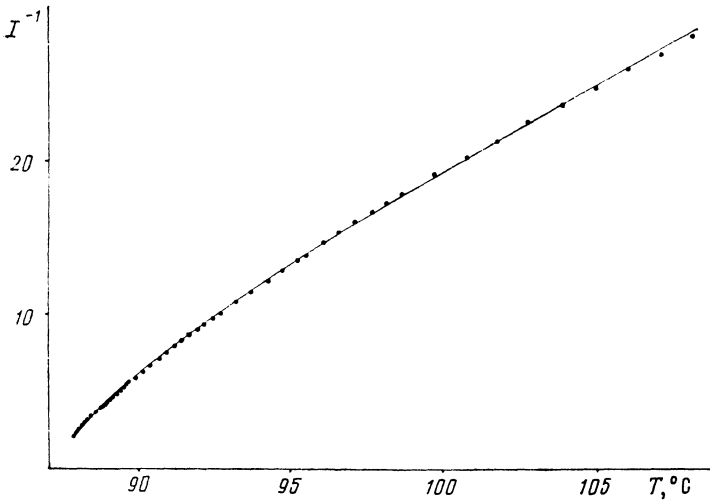


FIG. 10. Temperature dependence of the inverse light-scattering intensity (in arbitrary units) in the isotropic phase of $\bar{60} \bar{12}$ (Ref. 13). Curve—approximation by Eq. (10); $A_R = 10^{-5}$ (compare with $A_R/a \approx 5 \cdot 10^{-5}$ in Ref. 13).

the nematic mesophase exceeds 23 K ($\bar{608}$) the smectic-fluctuation contribution in the immediate vicinity of the $I-N$ transition reaches 3%.

DISCUSSION

The experimental data for the entropy jump $\delta S_{IN}/R$ on the $I-N$ transition line and for the smectic-fluctuation heat capacity $\delta C_{sm}/R$ were compared with expressions (8) and (9) independently. If the results are mutually consistent, the constants A , A_1 , and A_2 of the theory, obtained from the approximation of $\delta S_{IN}/R$ and $\delta C_{sm}/R$, should coincide. It is seen from Table I, however, that the difference between the coefficients A_2 noticeably exceeds their errors. The cause of this discrepancy may be failure to take into account, in the analysis of the smectic fluctuations, their interaction with the nematic fluctuations. We have approximated the entropy jump by expression (8) with coefficients A , A_1 , and A_2 obtained by reduction of the data on $\delta C_{sm}/R$. The result is shown as the broken trace in Fig. 5. The description of the experimental data differs little in this case from a direct comparison with (8), and remains adequate.

Let us examine now the agreement between the results of the calorimetric investigation and the light-scattering experiments. Allowance for interaction between nematic and smectic fluctuations renormalizes the nematic susceptibility in the isotropic phase, and remains predominant at small widths of the nematic mesophase. The reciprocal I^{-1} of the scattered-light intensity can then be expressed approximately in the form⁶

$$I^{-1} = a\tau - A_R \bar{\Delta}^{-4.5} \quad (10)$$

Figure 10 shows the temperature dependence of I^{-1} (Ref. 13) in the isotropic phase of $\bar{60} \bar{12}$. The solid curve is

an approximation of these data by the expression (10), using the constants A , A_1 , and A_2 obtained from the heat capacity of the smectic fluctuations $\delta C_{sm}/R$. The agreement is good in the entire temperature range.

The foregoing results, in our opinion, demonstrates convincingly the existence of uniaxial-smectic-mode fluctuations (crystallization fluctuations) in the isotropic phase. Direct proof is provided by the anomalous growth of the entropy jump $\delta S_{IN}/R$ on the $I-N$ transition line when the width of the nematic mesophase is decreased, and the agreement of this jump with the prediction (3) of the theory. It was more difficult to distinguish in the total isotropic-phase heat capacity the part due to the smectic fluctuations. However, the satisfactory agreement between the identified smectic-fluctuation heat capacity and the theoretical prediction, under perfectly reasonable assumptions, and the mutual consistency of independent calorimetric and optical experiments serve as additional arguments in favor of the proposed physical picture of the phenomenon.

In conclusion, we thank M. A. Anisimov, E. E. Gorodetskiĭ, and V. É. Podnek for help with the reduction of the experimental data.

¹Physicotechnical Institute of the Tadzhik SSR.

² $\bar{608}$, $\bar{60} \bar{10}$, and $\bar{60} \bar{12}$ are respectively 4*n*-hexyloxyphenyl-4*n*'-(octyl, decyl, dodecyl)-oxybenzoate. The samples were synthesized and purified by B. M. Bolotin ($\bar{608}$ and $\bar{60} \bar{12}$) and by D. Demus ($\bar{60} \bar{10}$). The possible impurity content, which we estimated from the width of the two-phase region of the $I-N$ transition, was less than 0.2% for all substances.

³E. E. Gorodetskiĭ and V. É. Podnek, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 244 (1985) [JETP Lett. **41**, 298 (1985)].

⁴L. D. Landau, Zh. Eksp. Teor. Fiz. **7**, 627 (1937).

⁵H. J. Coles and C. Strazielle, J. de Phys. **40**, 895 (1979).

- ⁴M. A. Anisimov, V. I. Labko, *et al.*, *Mol. Cryst. Liq. Cryst.* **104**, 273 (1985).
- ⁵A. Cohin, C. Destrade, H. Gasparoux, and J. Prost, *J. de Phys.* **44**, 427 (1983).
- ⁶M. A. Anisimov, E. E. Gorodetskiĭ, and V. E. Podnek, *Pis'ma Zh. Eksp. Teor. Fiz.* **37**, 352 (1983) [*JETP Lett.* **37**, 414 (1983)].
- ⁷M. A. Anisimov, V. I. Labko, *et al.*, *ibid.* **45**, 88 (1987) [**45**, 111 (1987)].
- ⁸S. A. Brazovskii, *Zh. Eksp. Teor. Fiz.* **68**, 175 (1975) [*Sov. Phys. JETP* **41**, 85 (1975)].
- ⁹M. A. Anisimov, V. P. Voronov, *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **45**, 336 (1987) [*JETP Lett.* **45**, 425 (1987)].
- ¹⁰V. P. Voronov, Abstracts, 10th All-Union Conf. on Problems of Calorimetry and Chemical Thermodynamics, Moscow Univ. Press, 1984, Vol. 2, p. 575.
- ¹¹S. B. Ranavare, V. G. K. M. Pistpati, and J. H. Freed, *Chem. Phys. Lett.* **140**, 225 (1987).
- ¹²M. F. Achard, G. Sigand, and F. Hardouin, *Liq. Cryst. of One- and Two-Dimensional Order*, **11**, 149 (1980).
- ¹³G. L. Nikolenko, Candidate's dissertation, Leningrad Univ., 1987.

Translated by J. G. Adashko