

Critical behavior of specific heat in a smectic-nematic phase transition in the liquid crystal octylcyanobiphenyl (8 CB)

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(Submitted 3 February 1983)

Pis'ma Zh. Eksp. Teor. Fiz. **37**, No. 8, 355–358 (20 April 1983)

Precision measurements of the specific heat C_p of the liquid crystal 8 CB are performed. Combined analysis of the temperature dependence of C_p in the nematic phase in the smectic- A -nematic phase transition and nematic-isotropic liquid phase transition permitted separating these anomalies and determining the critical indices of the specific heat. It is shown that the region of the smectic- A -nematic phase transition studied experimentally is the region of the transition from tricritical to critical behavior.

PACS numbers: 64.70.Ew, 65.40.Em

The nature of the phase transition between the smectic A (A) and nematic (N) phases has never been completely clarified. Since formation of a one-dimensional wave in the three-dimensional liquid ($d = 3$) is described by a two-component order parameter ($n = 2$), the phase transition $A \leftrightarrow N$ must belong to the same universality class ($d = 3, n = 2$) as the λ transition in liquid helium.¹ Interaction of the orientational and translational order parameters in the A phase leads to the appearance of a first-order phase-transition line for $A \leftrightarrow N$ and a tricritical point (TCP) on the temperature-pressure state diagram in homologous series of liquid crystals (LC) as well.^{1,2} The actual picture is slightly more complicated. The magnitudes of the critical indices (CI) for the specific heat $\alpha = 0.1-0.5$ differ from the value α predicted by the helium analogy (see Refs. 3 and 4 and the references cited there). The critical index α , as well as the CI for the correlation length measured in a direction parallel (ν_{\parallel}) and perpendicular (ν_{\perp}) to the orientation of the director depends on the width of the region of the N phase: $\Delta = (1 - (T_{NA}/T_{NI}))$. In addition, $\nu_{\parallel} \neq \nu_{\perp}$.³ The observed characteristics of the critical behavior of LC near the phase transition $A \leftrightarrow N$ could be related to the proximity of these transitions to TCP. To check this proposition, we studied the liquid crystal 8 CB, which has a narrow region of N phases ($\Delta = 0.022$) and lies on the line of the phase transition $A \leftrightarrow N$ near the TCP.^{4,5}

The 8 CB specimen was provided by P. V. Adomenas (Vil'nyus State University). The C_p measurements were performed using an improved adiabatic technique.⁶ The results of the measurements are shown in Figs. 1 and 2. In studying the phase transition $A \leftrightarrow N$, there were no hysteresis phenomena, and the quasistatic thermograms with the rate of change of temperature $\lesssim 3 \times 10^{-2}$ K/h did not reveal any steps or breaks characteristic for a δ function of the specific heat, and the times for establishing equilibrium after heating remained essentially unchanged. All of this permits classifying the phase transition $A \leftrightarrow N$ in 8 CB as a second-order phase transition. According to our estimates, the magnitude of the possible entropy jump with the phase transition

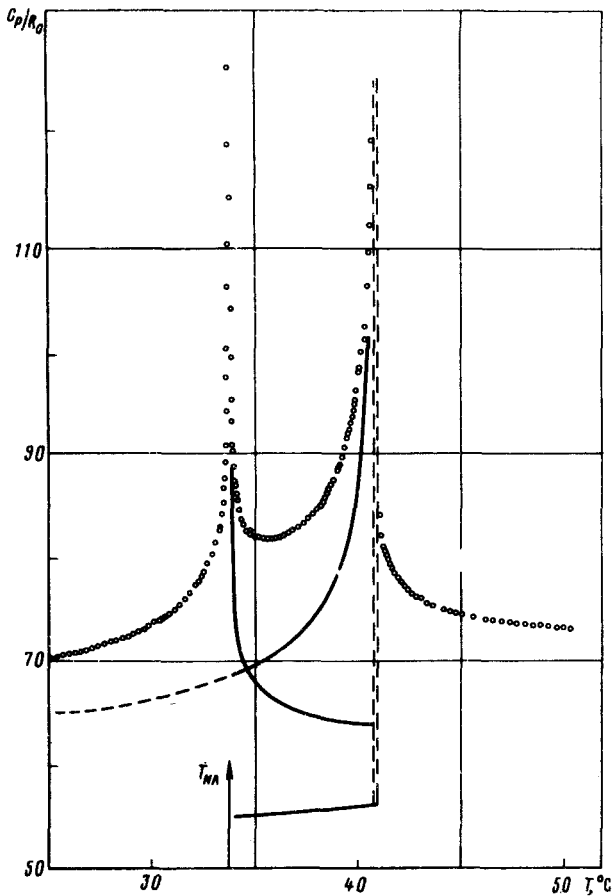


FIG. 1. Specific heat of the liquid crystal 8 CB in smectic A , nematic, and isotropic (I) phases; R_0 is the universal gas constant, $T_{AN} = 306.95$ K, $T_{NI} = 314.07$ K. The continuous lines show the anomalies of the specific heat with the phase transitions $A \leftrightarrow N$ and $N \leftrightarrow I$ and the regular part of the specific heat in the N phase, separated with the help of the model (2). The dashed lines show the two-phase region with width 0.18 K in the first-order transition $N \leftrightarrow I$; the corresponding entropy jump is $-0.29R_0$.

$A \leftrightarrow N$ in 8 CB does not exceed $10^{-3}R_0$ with the width of the region of the first-order phase transition $\leq 10^{-2}$ K. In the liquid crystal OOHCS studied by us previously⁶ ($\Delta = 0.0036$), the phase transition $A \leftrightarrow N$ was a first-order transition. Taking into account our data on 8 CB, as well as the data in Refs. 4 and 7–10, the TCP on the phase-transition line of the transition $A \leftrightarrow N$ can be referred to the quantity $0.02 < \Delta < 0.01$, consistent with the estimates of Ref. 5.

The measurements of the specific heat in 8 CB were initially approximated by a step function, containing a singular (ΔC_p) and a regular part:

$$\frac{C_p}{R_0} = \Delta C_p + A_1 + A_2 |\tau| \quad (1)$$

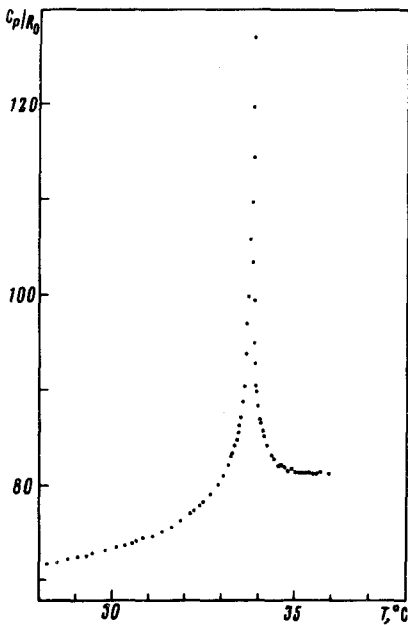


FIG. 2. Temperature dependence of the specific heat of 8 CB near the smectic-*A*-nematic phase transition.

In the *A* and *I* phases, the following expression was used for ΔC_p : $\Delta C_p = (T/T_0) A_0 |\tau|^{-\alpha}$, $\tau = T - T_0/T_0$ (in general $T_0 \neq T_c$). In the nematic phase, the singular part of the specific heat was taken in the form:

$$\Delta C_p = (T/T_0)(A_{01} |\tau|^{-\alpha_1} + A_{02} |\tau|^{-\alpha_2}),$$

where the indices 1 and 2 relate, respectively, to the phase transitions $A \leftrightarrow N$ and $N \leftrightarrow I$. This procedure permits making a realistic estimate of the magnitude of the anomaly in the specific heat for the phase transition $A \leftrightarrow N$ against the background of the orientational transition $N \leftrightarrow I$, which is especially important in the case of a phase transition with small Δ . In addition, the analysis no longer has to include points that are very close to T_c ($|\tau| \simeq 10^{-5} - 10^{-4}$), which generally lie in a region distorted by nonequilibrium "frozen" impurities.¹¹

We determined the parameters of the model (1) A_i , $i = 0, 1, 2$, α , T_0 and their confidence intervals with competence probability 0.68 by nonlinear regression analysis of the data.⁶ The results of the analysis are presented in Table I.

The critical index $\alpha \simeq 0.29$ for the *A* phase agrees well with the results of previous work on 8 CB: $\alpha \sim 0.25 - 0.31$.^{4,7-10} The intermediate values of the critical index α for the phase transition $A \leftrightarrow N$ (between $\alpha = 0.5$ for the tricritical point¹² and $\alpha \simeq 0$ for the universality class $d = 3$, $n = 2$) suggest that the experimental temperature range lies in the region of the transition from tricritical to critical behavior. In this case, the anomalies of the thermodynamic quantities are described by some effective critical indices, whose magnitude depends on how close T_c is to TCP and on the trajectory along

TABLE I.

LC phase	$T_0(\delta T_0)$	$\alpha(\delta \alpha)$	$A_0(\delta A_0)$	$A_1(\delta A_1)$	$A_2(\delta A_2)$	$\tau_{\max} / \tau_{\min}$
<i>A</i>	306.96 (0.04)	0.29 (0.06)	3.39 (1.12)	61.36 (3.13)	24.75 (12.52)	$2.8 \times 10^{-2} / 2 \times 10^{-4}$
<i>N</i>	306.96 (0.01)	0.23 (0.02)	3.54 (0.71)	55.14 (5.06)	81.70 (70.60)	$2.2 \times 10^{-2} / 2 \times 10^{-4}$
<i>N</i>	314.16 (0.04)	0.42 (0.09)	2.76 (0.98)	55.14 (5.06)	81.70 (70.60)	$2.2 \times 10^{-2} / 5 \times 10^{-4}$
<i>I</i>	313.96 (0.15)	0.30 (0.26)	2.18 (0.32)	65.75 (9.39)	12.25 (4.69)	$3 \times 10^{-2} / 5 \times 10^{-4}$

which T_c is approached.^{12,13} To check this proposition, the experimental data were analyzed to see if they agree with the model describing the behavior of the specific heat in the transition region¹³:

$$\Delta C_p = \frac{T}{T_0} \frac{1}{B_1 |\tau|^{1/2} + B_2 |\tau|^\alpha} \quad (2)$$

Equation (2) leads to tricritical behavior for large values of τ and to critical behavior for $\tau \rightarrow 0$. For fixed values $\alpha = 0.01-0.05$, the model (2) adequately describes the function $C_p(T)$ both in the *A* and *N* phases. The second term in the denominator in (2) becomes equal to the first term at $\tau^* \simeq 10^{-3}$, and therefore, the entire experimentally studied temperature range is the transition range (crossover region). Near T_c the critical behavior plays the dominant role; this explains the symmetrical nature of anomalies in C_p described by the model (1) in the *A* and *N* phases ($A_{0A}/A_{0N} \simeq 1$).

We obtained analogous results for the liquid crystal octyloxycyanobiphenyl (80 CB). An analysis based on the model (1) gives in the *A* and *N* phases the value $\alpha \simeq 0.25$. Based on the model (2), an adequate description of the *A* phase was obtained with $\alpha = 0.01-0.05$. In this case, $\tau^* \simeq 10^{-2}$, which corresponds to the increase in the width of the critical region.

The proposed interpretation of the phase transition $A \leftrightarrow N$ explained some heretofore incomprehensible experimental results such as the dependence of the critical indices α, ν_{\parallel} and ν_{\perp} on the magnitude of the temperature interval used to approximate the experimental data and on the width of the nematic gap Δ . A characteristic feature of the phase transition line for the transition $A \leftrightarrow N$ is the fact that the direct correlation radii $r_{0\parallel}$ and $r_{0\perp}$ ($r_c = r_0 \tau^{-\nu}$) increase with increasing Δ .³ As a result, Ginzburg's criterion determining the boundary between the critical and classical (TCP) behavior, $|\tau| \gg T_c^2 b^2 / (a')^4 r_{0\perp}^4 r_{0\parallel}^2$ (a' and b are coefficients in the corresponding Landau expansion), depends in a complicated manner on the quantity Δ , just as the coefficient b , and the direct-correlation radii $r_{0\parallel}(r_{0\perp})$ are functions of the width of the nematic phase.

This circumstance apparently determines the characteristics of the crossover phenomena on the nematic-smectic-*A* phase transition line.

We thank P. V. Adomenas for providing the liquid crystals for the experiment and M. A. Anisimov, V. M. Zaprudskii, and S. A. Pikin for fruitful discussions.

¹P. G. de Gennes, *Mol. Cryst. Liq. Cryst.* **21**, 49 (1973).

²W. L. McMillan, *Phys. Rev. A* **4**, 1238 (1971); **6**, 936 (1972).

³J. D. Litster, C. W. Garland, K. J. Lushington, and R. Schaetzing, *Mol. Cryst. Liq. Cryst.* **63**, 145 (1981).

⁴J. Thoen, H. Marynissen, and W. Van Dael, *Phys. Rev. A* **26**, 2886 (1982).

⁵M. A. Anisimov, *Pis'ma Zh. Eksp. Teor. Fiz.* **37**, 11 (1983) [*JETP Lett.* **37**, 11 (1983)].

⁶N. V. Arutyunyan, Yu. Yu. Daugvila, B. I. Ostrovskii, A. S. Sonin, E. L. Sorkin, B. A. Strukov, and S. A. Taraskin, *Fiz. Tverd. Tela* **23**, 1373 (1981) [*Sov. Phys. Solid State* **23**, 802 (1981)].

⁷G. B. Kasting, C. W. Garland, and K. J. Lushington, *J. Physique* **41**, 879 (1980).

⁸J. D. Le Grange and J. M. Mochel, *Phys. Rev. A* **23**, 3215 (1981).

⁹I. Hatta and T. Nakayama, *Mol. Cryst. Liq. Cryst.* **66**, 97 (1981).

¹⁰D. Brisbin, R. de Hoff, T. E. Lockhart, and D. L. Johnson, *Phys. Rev. Lett.* **43**, 1171 (1979).

¹¹M. A. Anisimov, *Usp. Fiz. Nauk* **114**, 249 (1974) [*Sov. Phys. Usp.* **17**, 722 (1975)].

¹²E. K. Riedel and F. J. Wegner, *Phys. Rev. B* **9**, 294 (1974).

¹³M. A. Anisimov, E. E. Gorodetskii, and V. M. Zaprudskii, *Usp. Fiz. Nauk* **133**, 103 (1981) [*Sov. Phys. Usp.* **24**, 57 (1981)].

Translated by M. E. Alferieff

Edited by S. J. Amoretty