Anomaly of the specific heat and the nature of the phase transition from an isotropic liquid to a nematic liquid crystal

M. A. Anisimov, S. R. Garber, V. S. Esipov, V. M. Mamnitskiĭ, G. I. Ovodov,
L. A. Smolenko, and E. L. Sorkin

All-Union Research Institute of Physico-technical and Radio Engineering Measurements

(Submitted December 28, 1976)
Zh. Eksp. Teor. Fiz. **72**, 1983–1993 (May 1977)

The temperature dependence of two substances (MBBA and BMAB) is studied near the isotropic liquid–liquid crystal phase transition. The phase transition possesses properties of transitions of both first and second order. It is shown that the results of previous work are distorted by the specific-heat δ-function smearing which is characteristic of transitions of first order. The main cause of the diffuseness are nonequilibrium impurities. Analysis of the temperature dependence of the specific heat shows that the fluctuations of the order parameter are not small at the transition point and that the Landau expansion is insufficient for a quantitative description of the pre-transition phenomena.

PACS numbers: 65.40.Hq

1. INTRODUCTION

At the present time interest is increasing in the extensively observed in nature first-order phase transitions with small values of the jumps in the entropy and volume. The closeness of such phenomena to second-order transitions allows us to expect a significant increase in the fluctuations and, consequently, in the appearance of a universality region. The reasons for the appearance of a discontinuity in the order parameter Q at the transition point is explained phenomenologically by means of an expansion of the thermodynamic potential Φ in powers of Q in the Landau theory[1]:

$$\Phi-\Phi_0={}^1/_2AQ^2-{}^1/_3BQ^3+{}^1/_4CQ^4+\ldots \qquad (1)$$

The possibility of the existence of a cubic term is associated with the character of the symmetry of the order parameter (for example, if Q is a tensor). In this case, the transition is a first-order transition. Then only an isolated critical point can exist on the transition line (the intersection with the line $B=0$). If $B \ll 1$, the transition is by definition, close to a second-order transition.

Another cause of a first-order transition is the negative sign of the constant C. Change in the sign of C can take place because of the interaction of Q and some additional order parameter. A characteristic example is the tricritical point of the mixture He^3–He^4, which divides the lines of superconducting transitions of the first and second order. In similar cases the closeness of the first-order transition ($C<0$) to the second ($C>0$) indicates closeness to tricritical point ($C=0$).

The theoretical investigation of the role of fluctuations in isolated[2] and tricritical[3] points show that the character of the singularities of the thermodynamic quantities is completely different in them. Therefore the study of the fluctuation phenomena near the first-order phase transitions can reveal the physical reasons for their closeness to the second order.

The phase transition from an isotropic liquid to a nematic liquid crystal is customarily described within the framework of the Landau theory. The tensor character of the order parameter leads to the existence of a cubic term in the expansion (1) and, consequently, to a transition of first order. The flucutuations in this case can be taken into account in the Ornstein-Zernike approximation[1] as corrections to the regular parts of the thermodynamic quantites. Experiments on double refraction, light scattering, and ultrasonic absorption[4–6] would appear to agree on whole with such an approach. However, the possibility of the description of this phenomenon in the approximation of the self-consistent field is an astonishing one, since the intermolecular forces responsible for the transition are essentially short-range forces. In the vicinity of the critical point of liquids there is, for this reason, no region where the self-consistent field approximation is valid.[7]

Analysis of the character of the singularity of the specific heat could serve to clarify this situation. Unfortunately, the results of all three investigations of the specific heat of the same nematic liquid crystal—MBBA[8–10]—published in recent years, differ so widely from one another that they do not allow even qualitative common interpretation. In this paper we present the results of the investigation of the specific heat of two nematic liquid crystals: *n*-methoxy-*n*′ benzylidene butylaniline (MBBA) and *n*′-*n*-butyl-*n*′ methoxyazoxybenzene (BMAB). The character of the anomalies of the specific heats in the two cases is exactly the same. The principal reason producing the distortion of the ideal dependence is the existance of nonequilibrium (frozen) impurities. The analysis of the temperature dependence of the specific heat showed that the fluctuations of the order parameter are not small at the transition point and the expansion (1) is insufficient for the quantitative description of the pretransition phenomena.

2. EXPERIMENTAL PART

The samples of MBBA and BMAB were kindly supplied us by E. I. Kovshev and V. T. Lazarev (Scientific Research Institute of Organic Intermediate and Dyestuffs).

0038-5646/77/4505-1042$02.40

The synthesis and purification of the materials are described in Ref. 11. BMAB is a mixture of two isomers of approximately equimolecular composition. The material is not hygroscopic. Addition purification of the BMAB was not performed by us. Additional purification of the MBBA was done by the blowing dry argon for several hours which, however, did not lead to any significant increase in the bleaching temperature (318.45 K), the calorimeters were charged in an atmosphere of dry nitrogen.

The shift of the transition temperature T_t isotropic liquid-nematic liquid crystal was also studied visually as a function of the impurity content: benzene, naphthalene, n-hexane, cyclohexane, carbon tetrachloride (in MBBA) and n-heptane, isooctane, n-dodecane, n-heptadecane (in BMAB). In the MBBA solutions, only the bleaching temperature T_t^+ was fixed and in the BMAB solutions, the temperature of disappearance of the isotropic phase T_t also (Fig. 1). The initial parts of both curves $T_t(x)$ are practically identical and the derivative dT_t/dx for both MBBA and BMAB and amounts to 2 ± 0.2 (K/mol%). By knowing ΔT—the decrease in the transition temperature, and Δx—the difference in concentrations of the isotropic and nematic phases, we can estimate the heat of transition λ of the pure sample by the well-known "cryoscopic" formula (see Ref. 1):

$$\lambda \approx RT^2 \, \Delta x/\Delta T. \qquad (2)$$

For BMAB the value of λ/RT_t is obtained in the range from 0.15 to 0.2 depending on the type of impurity, which is characteristic in order of magnitude for the isotropic liquid–liquid crystal transitions.

The specific heat was measured by the adiabatic method[12] with the improvements described in Ref. 13. In the calorimetric experiment close to the critical points of the liquids,[12] stirring has traditionally been used to ensure spatial homogeneity of the sample and a decrease in the time for establishing thermodynamic equilibrium. However, there was no corresponding experience with liquid crystals, and it was not clear beforehand how important the similar effect of stirring would turn out to be (for example, the possible hydrodynamic ordering). Therefore calorimeters of two types were prepared: the first was a container of stainless steel, provided with a magnetic stirrer and covered by a layer of copper (0.5 mm), the second was of copper—a "bookcase" placed in a cylindrical housing (Fig. 2). Such construction permitted us to reduce the time of equalization of the temperature to 1–2 min far from the transition point in the absence of stirring. The specific heat of MBBA was measured in both calorimeters and that the BMAB in the steel calorimeter, both with and without stirring.

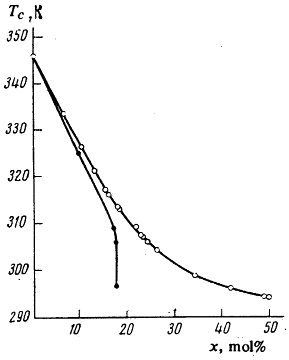

FIG. 1. Dependence of the temperature of appearance of the nematic phase (open circles) and the temperature of the disappearance of the isotropic phase on the concentration of n-heptadecane in BMAB.

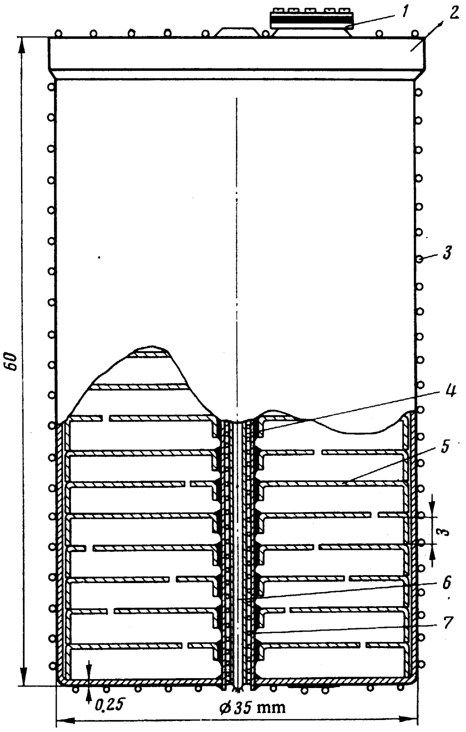

FIG. 2. Copper calorimeter—"bookcase": 1—collar for filling, 2—cover, 3—arm of bridge temperature sensor, 4—sleeve of heating unit, 5—heat exchanging disks, 6—platinum resistance thermometer, 7—manganin heater.

Figure 3 shows the results of the measurements over the entire temperature range studied, with the excep-

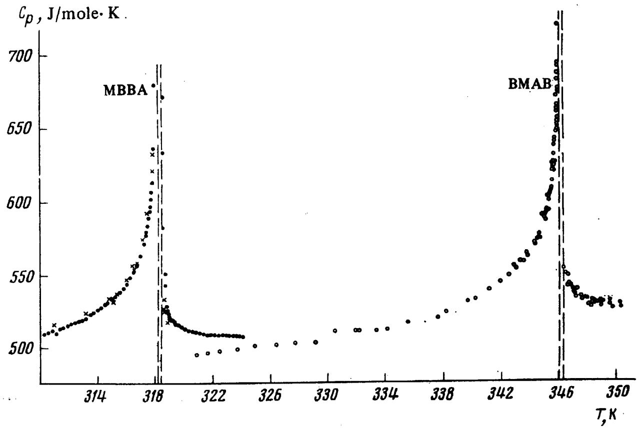

FIG. 3. Specific heat of MBBA and BMAB. The results of measurements of C_p of MBBA with stirring are indicated by the asterisks. The results of the measurements of C_p of MBBA directly in the transition region are shown in Fig. 4. The dashed lines indicate the temperatures of beginning and end of the transition.

tion of the narrow region immediately adjoining the transition temperature (0.2 K for BMAB and 0.6 K for MBBA). The temperature dependences of the specific heat in both samples were similar. With the exception of the region immediately adjoining the transition temperature, the mean random error in the measurements without stirring amounted to ~ 0.05%. In the measurements with stirring, it was an order of magnitude greater, which, in particular, is due to the small ratio of the specific heat of the sample to that of the calorimeter (~ 30%). At the same time, the errors in the measurements with stirring were practically independent of the closeness of the transition point, while, without stirring, in the narrow range (0.2–0.3 K) near the transition, the scatter amounted to several dozen percent.

Figure 4 shows the results of measurements of the specific heat of MBBA in the region immediately adjoining the transition. In the measurements without stirring, the change in temperature by 0.1 K from 318 to 318.1 K, and the corresponding decrease of it from 318.9 K to 318.8 K leads to an increase in the time of equilization of the temperature from 1 to 5–6 hours. Upon further approach to the transition, the equalization times exceeded ten hours and more, and it was in principle impossible to obtain equilibrium results without stirring. On the other hand, the equalization times, in the measurements with stirring, remained small everywhere (of the order of a few minutes) so far as one could judge from the temperature behavior of the calorimeter.

The results obtained with stirring and without are easily understood if we take into account the presence of impurities ~ 1% in the sample studied. Simplifying the problem, we shall consider impurities of a single type. Qualitatively, the picture does not change in the presence of several different impurities. The character of the distortion of the specific heat anomaly of the contaminated sample depends essentially on whether the impurities are in thermodynamic equilibrium or not.[7] The equilibrium impurities break up the transition. In this case, we can speak of the initial temperature (T_t^+) of the transition and the final temperature (T_t^-) of the transition from the disordered phase to the ordered phase. In MBBA, $T_t^+ - T_t^- = 0.28$ K, which corresponds to an impurity content ~ 1% (see Fig. 1); in BMAB, $T_t^+ - T_t^- = 0.20$ K. In the latter, the two-component character of the sample (isomerism) makes its own contribution to the "breaking up" of the transition. In an absolutely pure and homogeneous sample, the transition point corresponds to a δ function in the specific heat. The presence of a small amount of equilibrium impurities, distributed uniformly over the sample transforms the δ function into a narrow trapezoid (measurements with stirring in Fig. 4). The specific heat of the two-phase system ($T_t^- < T < T_t^+$) is a linear function of the temperature in first approximation. The area of the trapezoid, measured off from the regular part of the specific heat, is the heat of transition. The values of the transition temperature and specific heat thus obtained are given in Table I for both samples.

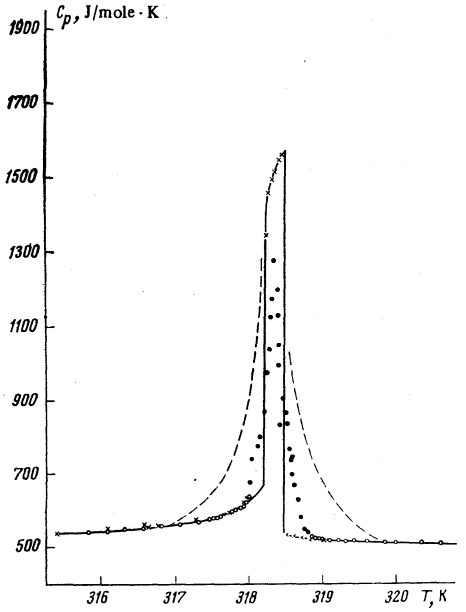

FIG. 4. Specific heat of MBBA in the transition region of isotropic liquid—liquid crystal: × measurements with stirring, ●—results of measurements with times of equalization of more than 5–6 hrs., o—measurements without stirring with equalization times less than 5 hrs. Dashed curves—results obtained in Ref. 10, smoothed and reduced to our value of the transition temperature.

TABLE I.

	T_{cl}^+, K	T_{cl}^-, K	λ/RT_{cl}	λ/RT_{cl} [4]
MBBA	318.47	318.19	0.11±0.01	0.15
BMAB	346.25	346.05	0.12±0.01	–

Nonequilibrium and therefore non-uniformly distributed impurities distort the δ function in another manner. Different parts of the sample have their own initial and final transition, depending on the concentration of the impurities and the δ function is smeared out ("wings" appear). The results can be reproduced if the relaxation time of the nonuniformities is much greater than the time of measurement.

In light of what has been said, it is easy to understand the results of Ref. 10 and of our measurements without stirring (Fig. 4). We only note that the width of the diffusion of the δ function in Ref. 10 amounts to ~ 3 K (i.e., three times greater than in our case). Such a strong diffusion is evidently connected with the features of the calorimeter construction used in Ref. 10—a long (~ 50 mm) glass ampoule with an axial aperture and a heater. In such a construction, a significant temperature gradient is possible over the height and a corresponding nonuniform distribution of the impurities.

In addition to the δ-function diffusion, its breaking up into two peaks was also observed in Ref. 9. The peaks were separated by about 0.2 K. Several peaks have repeatedly been observed in investigations of phase transitions in mixtures (see, for example, Ref. 14). They can arise if in the nonuniform distribution of the impurities there exist in the sample parts of noticeably different concentration. In order to verify the assumption on the role of the "frozen" impurities and to explain the mechanism of the onset of giant temperature equalization times near the transition, we made visual observations of the MBBA in an optically thermostated cell, equipped with an MBS-1 microscope. The drift rate of the temperature was 10^{-2}K/hr. The beginning of the transition into the nematic phase was characterized by the sudden appearance throughout the volume of spherical drops of radius $(2-3)\times10^{-3}$ cm. As the temperature decreased, the drops grew in size, but this growth was always limited to a radius of $(2-3)\times10^{-2}$ cm. After reaching the maximum size, the picture did not change over a period of many hours, in spite of the temperature drift. Such a two-phase state is possible only because of the presence of impurities in the sample. The impurity content in the bubbles host solution is different. In a temperature change, the equilibrium concentration of impurities was established very slowly by the diffusion method, i.e., without stirring. The stabilization of the dimensions of the bubbles indicated that the impurity concentration in them was far from equilibrium.

Thus, in the region adjoining the transition region, measurements without stirring lead to a distortion temperature dependence of the specific heat, while the character of the diffusion of the δ function depends on the quantity, degree of nonequilibrium and the method of distribution of the impurities in the sample. The inclusion of such a distorted region[9,10] in the sample leads to a qualitatively invalid interpretation of the results.

3. REDUCTION OF THE MEASUREMENT RESULTS

The results of these measurements, which we have assumed to be equilibrium, were approximated by the power-law dependence assumed in the reduction of the experiments close to the critical points of liquids[7]:

$$\frac{C_p}{R} = \frac{T}{T_c} A_0\tau^{-\alpha}+A_1+A_2\tau, \tag{3}$$

where $\tau=(T-T_c)/T_c$ is the temperature of divergence of the specific heat T_c in the general case does not coincide with the transition temperature T_t. The results of the determination of the constants α, T_c, A_0, A_1, A_2 and their confidence intervals (68% probability) for the nematic phase of MBBA, put forth in Ref. 15, are given in Table II. Here y is some quantity obtained from the sums of the deviation and obeying the Fisher distribution, against which the hypothesis of the inadequacy of the chosen model of approximation can be verified.[15] At $y \geq F_{1-\alpha}(m,n)$ (m is the number of parameters, n is the number of points) the model is inadequate with probability $1-\alpha$, $F_{0.68}(m,\infty)\approx 1$, $F_{95}(5,\infty)\approx 2.2$.

TABLE II.

$-\lg\tau$	α ($\delta\alpha$)	T_c, K (δT_c)	A_0 (δA_0)	A_1 (δA_1)	A_2 (δA_2)	y
1–3	0.31 (0.05)	318.30 (0.03)	2.38 (0.94)	54.44 (1.35)	19.5 (9.9)	0.2
1.8–3	0.27 (0.08)	318.29 (0.04)	3.52 (2.51)	52.05 (4.49)	–4.32 (27.26)	0.1

TABLE III. Results of approximation of the temperature dependence of the specific heats of MBBA and BMAB by the expression (3) with fixed value of $\alpha=0.5$.

$-\lg\tau$	T_c (δT_c)	A_0 (δA_0)	A_1 (δA_1)	A_2 (δA_2)	y	τ_c^*
	Isotropic phase of MBBA					
1.6–2.6	318.10 (0.07)	0.204 (0.016)	58.80 (0.20)	35.7 (4.3)	0.5	$1.15\cdot10^{-3}$
	Nematic phase of MBBA					
1–3	318.43 (0.01)	0.597 (0.008)	58.87 (0.09)	49.9 (2.1)	1.3	$7.4\cdot10^{-4}$
	Isotropic phase of BMAB					
1–3.5	345.97 (0.17)	0.15 (0.04)	61.6 (0.6)	36.4 (18.9)	0.6	$8.2\cdot10^{-4}$
	Nematic phase of BMAB					
1.8–2.8	346.18 (0.05)	0.65 (0.06)	60.1 (0.8)	40.0 (30.2)	0.02	$3.8\cdot10^{-4}$

$^*\tau_c = |(T_t - T_c)/T_c|$.

We call attention to two circumstances. First, the value of the exponent α in the approximation with the free parameters α, A_0, A_1, A_2 and T could be chosen only in a single case—the nematic phase of MBBA. In BMAB, because of the large error, and in the isotropic phase of MBBA, because of the smallness of the effect, the dispersion α exceeds its mean value. Such a negative result should not be surprising. As a rule, the values of the critical exponents published in the literature at fixed values of T_c and the regular part, and the confidence interval shown, starting from the intuitive considerations of the authors. In the second case, which follows from the expansion (1) for the ordered phase, the value $\alpha=0.5$ lies beyond the limits of the confidence interval. At attempt to describe the specific heat in the nematic phase of MBBA by the expression (3) with fixed $\alpha=0.5$ leads to the value $y=1.3$ (Table III), which means inadequacy of the model with probability >68%.

4. DISCUSSION

The value of the exponent $\alpha<0.5$, obtained for the nematic phase of MBBA, can correspond to the transition from the region of applicability of the self-consistent field approximation to the critical region.[2] Another possibility is the effective decrease in the exponent due to the effect of the impurities. Such a possibility seems less probable to us, since estimates (true, very rough estimates) of the interval τ in which the effect of the impurities is significant,[7] give

$$\tau\leqslant\left[x\left(\frac{1}{T_t}\frac{dT_t}{dx}\right)^2\right]^{1/\alpha}\approx 10^4.$$

Unfortunately, the absence of sufficient accurate data for the isotropic phase of MBBA and for BMAB does not allow us to explain the values $\alpha\approx0.3$ unambiguously. Therefore, we have undertaken an attempt to reconcile the results of our and other variants of the expansion of the thermodynamic potential in the Landau theory, approximating the temperature dependence of the specific heat in all cases by the expression (3) with a fixed value $\alpha=0.5$ (Table III). Such an attempt seems timely to us, since the number of results (heat of transition, jump in the specific heat and the order parameter) does not depend or depends weakly on the method of approximation.

TABLE IV. Temperature values near a first order phase transition that is near the second order, for different variants of the expansion of the thermodynamic potential in powers of the order parameter.

$\Phi-\Phi_0$	Q_t	Q_c	τ_c^+	τ_c^+/τ_c^-	$A_0-\tau^{-\alpha}$	$A_1^- - A_1^+$
2–3–4	$\frac{2B}{3C}$	$\frac{3}{4}Qt$	$\frac{2B^2}{9aC}$	8	$\frac{B}{2C}\left(\frac{C}{a}\right)^{1/2}\tau^{-1/2}$	$\frac{a^2}{2C}$
2–4–6	$\left(-\frac{3C}{4D}\right)^{1/2}$	$\left(\frac{2}{3}\right)^{1/2}Qt$	$-\frac{3C^2}{16aD}$	3	$\frac{a}{4}\left(\frac{a}{D}\right)^{1/2}\tau^{-1/2}$	0
2–3–6	$\left(\frac{B}{2D}\right)^{1/3}$	$\left(\frac{1}{2}\right)^{1/3}Qt$	$\frac{1}{2}B\left(\frac{B}{2D}\right)^{1/3}$	$\frac{2^{4/3}}{3-2^{4/3}}$	$\frac{a}{4}\left[\frac{a}{D+(B/8Q_c^3)}\right]^{1/2}\tau^{-1/2}$	0
2–3–4–6	$\left(-\frac{3C}{4D}\right)^{1/2}+\frac{B}{3C}$	$\left(-\frac{C}{2D}\right)^{1/2}+\frac{B}{4C}$	$\frac{3C^2}{16\,aD}+\frac{B}{2a}\left(-\frac{3C}{4D}\right)^{1/2}$	$3\left\{1+\left[\frac{8}{9}-\left(\frac{2}{9}\right)^{1/2}\right]\cdot\frac{DB}{C^2}\left(-\frac{3C}{4D}\right)^{1/2}\right\}$	$\frac{a}{4}\left[\frac{a}{D+(B/8Q_c^3)}\right]^{1/2}\tau^{-1/2}$	0

Note. (2-3-4)→$\Phi-\Phi_0=\frac{1}{2}a\tau^*Q^2-\frac{1}{3}BQ^3+\frac{1}{4}CQ^4$; (2-4-6)→$\Phi-\Phi_0=\frac{1}{2}a\tau^*Q^2+\frac{1}{4}CQ^4+\frac{1}{6}DQ^6$ ($C<0$); (2-3-6)→$\Phi-\Phi_0=\frac{1}{2}a\tau^*Q^2-\frac{1}{3}BQ^3+\frac{1}{6}CQ^6$; (2-3-4-6)→$\Phi-\Phi_0=\frac{1}{2}a\tau^*Q^2-\frac{1}{3}BQ^3+\frac{1}{4}CQ^4+\frac{1}{6}DQ^6$ ($C<0$); Q_c is the jump in the order parameter at $\tau=0$, the point $\tau^*=0$ corresponds to a second-order transition at $B=0$ ($\tau^*=\tau+\tau_c^++\tau_c^-$); account of the term $\sim Q^5$ in the presence of the cubic term leads to insignificant corrections; in the variant 2-3-4-6 ($C>0$) all the quantities except the specific heat behave the same as in 2-3-4, with the linear corrections $\sim D$, while the formula for the specific heat is the same as in the variant 2-3-4-6 ($C<0$); for all variants $\lambda/RT_t=\frac{1}{2}aQ_t^2$.

If this attempt were successful, then the result $\alpha\approx 0.3$ for the nematic phase of MBBA could be regarded as accidential (for example, associated with some distorting factors).

The results of the calculation of the thermodynamic quantities for different variants of the expansion of the thermodynamic potential in powers of the order parameter are given in Table IV. The results of the first two columns of Table IV are well known: the 2–3–4 is traditionally used for the description of liquid crystals (see, for example, Ref. 4), the variant 2–4–6 ($C<0$) describes the first-order phase transition close to the tricritical point[1,3] (for example, the transition between the β- and δ-phases in the ammonium halides[16]). Table V gives the values of the constants of the expansion of the thermodynamic potential (in units of RT_t) and the coefficient A_0^-, calculated for MBBA from the experimental data: $Q=0.4$,[4] $\lambda=0.11RT_t$, $\tau_c^-=7.4\times10^{-4}$. In the variant 2–3–4–6 for the calculation of the constants, we used the experimental value $A_0^-=0.6$. The nearby values of the constants are obtained also for BMAB.

At first glance, the variant 2–3–4 gives satisfactory results: the value of the constants are close to those published in the literature,[4] the specific heat in the nematic phase is determined by the temperature dependence of the order parameter, and the calculated value does not differ greatly from the experimental, while the root dependence of C_p at $T>T_t$, which as a whole is connected with the fluctuations, can be obtained by taking into account the term $\sim(\nabla Q)^2$ in the expansion (1). However, a comparison between the right and left branches of the specific heat shows the contradiction of this variant and the experiment at three points.

1. In both MBBA and BMAB, the regular parts $A_1^-=A_1^+$, while the variant 2–3–4 predicts the jump $a^2/2C\approx 10R$.

2. The ratio τ_c^+/τ_c^- is 4–5 times smaller than the theoretical ratio.

3. The coefficient A_0^+ is 3–5 times greater than follows from the formula[17] $A_0^+=V_s/16\pi r_0^3$ (V_c is the molecular volume, r_0 the radius of the interaction; from experiments on light scattering, $r_0=5.5$ Å[4]–6.8 Å[5]), obtained for the fluctuation corrections to the specific heat in the self-consistent field approximation.

TABLE V. Constants of the different variants of the expansion of the thermodynamic potential calculated according to the experimental data for MBBA.

$\Phi-\Phi_0$	a	B	C	D	A_0^-
2–3–4	1.4	0.06	0.1	–	0.76
2–4–6 (C<0)	1.4	–	–0.06	0.26	0.79
2–3–6	1.4	0.01	–	0.11	0.99
2–3–4–6 (C<0)	1.4	0.001	–0.07	0.39	0.6 *
2–3–4–6 (C>0)	1.4	0.09	0.18	0.18	0.6 *

*Experimental value

Those variants are more acceptable which include the sixth order term, i.e., which take into account the smallness of the constant C. But the smallness of the constant C denotes the existence of a tricritical region.[1)] Actually, the Ginzburg criteria, which determine the region of applicability of the self-consistent field approximation, (see Ref. 2)

$$\tau>\left(\frac{V_c}{r^3}\right)^2\frac{C^2}{a^4} \qquad (4)$$

in the case of short-range interaction ($V_c/r_0^3\approx1$) and $C\ll1$ determine the tricritical point at the same time: $\tau>C^2/a^4$. In the triple point region, the results of the self-consistent field approximation are valid (with accuracy to within a logarithmic correction). In particular, the specific heat $C_p^{\pm}\sim\tau^{-1/2}\ln^{\mp1}\tau$.[3] For MBBA and BMAB, $C^2/a^4=10^{-2}-10^{-4}$ and the experimental interval τ is evidently located in the region of transition from tricritical behavior[3] to critical.[2] The existence of a term of third order far from the transition point leads only to corrections in the tricritical point behavior (Table IV). Finally, such behavior of the specific heat should be analyzed according to formulas obtained with account of fluctuations in the microscopic theory,[3] both above and below T_t, and therefore a comparison of experiment with any of the variants of the Landau expansion is, strictly speaking, invalid. Within the framework of this expansion, for example, it is generally impossible to explain the large amplitude of the anomaly of the specific heat in the isotropic phase. For a quantitative comparison with the results of theoretical researches[2,3] new, more accurate experimental data are necessary.

If the tricritical point behavior near the transition isotropic liquid–liquid crystal is confirmed, then this will be by showing the important role of the interaction of the tensor order parameter with other power methods.

In conclusion, we thank V. M. Malyshev for help in setting up the experiment, E. E. Gorodetskiĭ and V. M. Zaprudskiĭ for useful discussion.

1) Naturally, this does not mean that there exists a tricritical point on the line $T_t(P)$, in the same way as the smallness of the constant B does not require the necessary existence of an isolated critical point on this line.

---

[1] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics) Nauka, 1964. L. D. Landau, Sobranie trudov (Collected Works) Vol. 1. Nauka, 1969, pp. 123, 234.

[2] P. G. Vigman, A. I. Larkin, and V. M. Filev, Zh. Eksp. Teor. Fiz. 68, 1883 (1975) [Sov. Phys. JETP 41, 944 (1975)].

[3] E. E. Gorodetskiĭ and V. M. Zaprudskiĭ, Zh. Eksp. Teor. Fiz. 72, 2299 (1977) [Sov. Phys. JETP 45, No. 6 (1977)].

[4] T. W. Stinson and J. D. Lister, Phys. Rev. Lett. 25, 503 (1970); Phys. Rev. Lett. 30, 688 (1973).

[5] E. Gulary and B. Chu, Chem. Phys. 62, 798 (1975).

[6] L. K. Vistin' and V. I. Uchastkin, Zh. Eksp. Teor. Fiz. 70, 1 798 (1976) [Sov. Phys. JETP 43, 936 (1976)].

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

[8] J. Mayer, T. Waluga, and J. A. Janik, Phys. Lett. 41A, 102 (1972).

[9] K. Hirakawa and Sh. Kai, J. Phys., Japan 37, 1472 (1974).

[10] B. I. Ostrovskiĭ, S. A. Taraskin, B. A. Strukov, and A. S. Sonin, Zh. Eksp. Teor. Fiz. 71, 692 (1976) [Sov. Phys. JETP 44, 363 (1976)].

[11] V. V. Titov, Yu. N. Gerulaitis, V. T. Lazareva, K. V. Roĭtman, E. I. Balabanov, A. I. Vasil'ev, Yu. M. Bunakov, and M. F. Grebenkin, in Collected Papers of the Second All-Union Conference on Liquid Crystals and Symposium on their Practical Application, Ivanovo, 1973, p. 178.

[12] M. A. Anisimov, A. V. Voronel', and T. M. Ovodova, Zh. Eksp. Teor. Fiz. 61, 1092 (1971) [Sov. Phys. JETP 34, 583 (1972)].

[13] V. M. Malishev, materials of the 6th All-Union Conference of Calorimetry. Tbilisi, Metsniereba, 1973, p. 549.

[14] A. V. Voronel', V. G. Gorbunova, and N. G. Shmakov, Pis'ma Zh. Eksp. Teor. Fiz. 9, 333 (1969) [JETP Lett. 9, 195 (1969)].
ZhETF Pis. Red. 9, 333 (1969) [JETP Lett. 9, 195 (1969)].

[15] D. M. Himmelbau, Process Analysis by Statistical Methods, Wiley, 1970.

[16] E. B. Amitin, Yu. A. Kovalevskaya, and I. E. Paukov, Zh. Eksp. Teor. Fiz. 71, 700 (1976) [Sov. Phys. JETP 44, 368 (1976)].

[17] V. G. Vaks and A. I. Larkin, Zh. Eksp. Teor. Fiz. 49, 975 (1965) [Sov. Phys. JETP 22, 678 (1966)].

Translated by R. T. Beyer

Singularities of magnetic properties of doped $CdCr_2Se_4$ single crystals in the region of the Curie point

K. P. Belov, L. I. Koroleva, M. A. Shalimova, V. T. Kalinnikov, and T. G. Aminov

Moscow State University

(Submitted December 28, 1976)
Zh. Eksp. Teor. Fiz. 72, 1994–1999 (May 1977)

The dependence of the magnetization σ on the temperature T and on the magnetic field H was investigated in $CdCr_2Se_4$ single crystals doped with indium or copper and also having a selenium deficiency, in the region of the Curie point T_c and somewhat above it. The (H) curves at temperatures slightly exceeding T_c have a critical field in whose vicinity the magnetization increases jumpwise by 80%. In the same temperature region, a temperature hysteresis of σ was also observed. Annealing of a selenium-deficient sample in a selenium atmosphere decreases greatly the jump on the σ(H) curves and narrows down the temperature hysteresis. The indicated experimental facts can be attributed to the production of ferrons under the influence of the magnetic field at temperatures above T_c. The field-induced transition from the paramagnetic state to the ferron-containing state is an analog of a first-order phase transition.

PACS numbers: 75.30.Cr, 75.60.Nt, 75.30.Kz

In magnetic semiconductors, particularly $CdCr_2Se_4$, a strong exchange interaction exists between the carriers and the localized magnetic moments (s–d exchange). This exchange interaction leads to a number of singularities of the magnetic and electric properties of these semiconductors. It is presently customary to attribute the greater part of these singularities to the presence of special magnetic microregions characterized by an increased degree of ferromagnetic order—ferrons. For pure magnetic semiconductors, these microregions were theoretically predicted by Nagaev[1,2] and by von Molnar and Methfessel.[3] They have shown that owing to the s–d exchange it is energywise more convenient for the carriers to become autolocalized and