

# Investigation of the optical properties of liquid crystals near the point of transition from an isotropic liquid to a nematic liquid crystal

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An investigation was made of the temperature dependence of the intensity of the light scattered and transmitted by a BMOAB liquid crystal in the vicinity of its transition from the isotropic phase side. Calculations were made of the intensity of double scattering of light and of the extinction coefficient for the case when the order parameter is a tensor. Single scattering was separated from the total intensity and the temperature dependence of the scattering constant was determined. It was found that a deviation of the temperature dependence of the reciprocal susceptibility from linearity could not be explained by multiple scattering of light. The temperature dependences of the susceptibility and of the specific heat were analyzed using the Landau–de Gennes model in which terms up to the sixth order were included. It was found that the experimental dependences could be described only if the fluctuation corrections were included.

It is known that the intensity of scattered light increases strongly near the isotropic liquid–nematic liquid crystal transition.<sup>1,2</sup> In a fairly wide range of temperatures the reciprocal of the scattered-light intensity is practically a linear function of temperature. This is unusual for second-order phase transitions, because it corresponds to the critical index of the susceptibility amounting to unity. It may mean that, in a certain range of conditions, the Landau theory is applicable to the system in question. In the direct vicinity of the phase transition point the nature of the temperature dependence changes: the intensity begins to rise more rapidly with temperature.<sup>1,2</sup> The simplest cause of this behavior is an increase in the contribution of multiple scattering on approach to the transition point. The nonuniversal nature of the behavior may also indicate the onset of the fluctuation region where an interaction between fluctuations of the order parameter makes an important contribution to the susceptibility.<sup>3</sup> Finally, these fluctuations can interact with fluctuations with any other order parameter, for example, that associated with a smectic mesophase.<sup>4,5</sup>

Information on the critical behavior of nematic liquid crystals can also be obtained from other experiments, for example, from a determination of the temperature dependences of the specific heat and of the order parameter. However, a discontinuity at the first-order phase transition prevents extracting fairly complete information from each such experiment separately. For example, even when the specific heat is measured very accurately, the results are difficult to interpret because of indeterminacy of the value of the apparent temperature of the second-order phase transition. However, this temperature can be determined quite simply from optical data. Therefore, reasonably reliable conclusions can only be drawn from investigations of several properties at the same time.

We determined the intensity of light of different polarizations scattered singly or multiply by the isotropic phase of *p-n*-butyl-*p*-methoxyazoxybenzene (BMOAB) in a wide range of temperatures and we measured the intensity of the

transmitted light. The data on the specific heat,<sup>6</sup> temperature dependence of the order parameter,<sup>7</sup> and heat of transition<sup>8</sup> of this liquid crystal have already been published. We selected BMOAB also because it is characterized by a very wide (~50 °C) range of existence of the nematic phase and also because it does not have a smectic mesophase.

## 1. LIGHT SCATTERING IN AN ISOTROPIC PHASE OF A NEMATIC LIQUID CRYSTAL

An increase in the intensity of the scattered light in the vicinity of the transition point is due to an increase in fluctuations of the order parameter, which in this case is a symmetric tensor  $\hat{S}$  with a trace equal to zero. For our purpose it is convenient to select as  $\hat{S}$  the zero-trace part of the permittivity tensor at an optical frequency ( $\lambda = 6328 \text{ \AA}$ ). The intensity of light scattered singly by fluctuations of  $\hat{\epsilon}$  is

$$I_z^{z(1)} = \frac{2}{3} \frac{I_0 V R_{sc}}{R^2} G_z^z(q) e^{-\sigma L},$$

$$I_{xy}^{z(1)} = \frac{1}{2} \frac{I_0 V R_{sc}}{R^2} G_{xy}^z(q) e^{-\sigma L},$$
(1)

where  $G_z^z(0) = G_{xy}^z(0) = 1$  and

$$R_{sc} = \frac{\pi^2}{5\lambda^4} \langle \text{Sp } \delta \hat{\epsilon}^2 \rangle$$
(2)

is the scattering constant. The superscript represents the polarization of the incident light and the subscript the polarization of the scattered light;  $I$  is the intensity of the incident light traveling along the  $x$  axis;  $\mathbf{q}$  is the scattering vector;  $q = 2k \sin(\theta/2)$ ;  $k$  is the wave number of an electromagnetic wave in the investigated medium;  $\theta$  is the scattering angle in the  $xy$  plane;  $R$  is the distance from the observation point;  $V$  is the scattering volume;  $\sigma$  is the extinction coefficient;  $L$  is the path traveled by light in the medium. In the Ornstein-Zernike approximation the functions  $G_z^z$  and  $G_{xy}^z$  governing the angular dependence of the intensity of the scattered light are given by the expressions<sup>9,10</sup>

$$G_z^z(q) = \frac{1}{4} \left( \frac{3}{1+q^2 r_{c1}^2} + \frac{1}{1+q^2 r_{c2}^2} \right),$$

$$G_{xy}^z(q) = \frac{1}{2} \left( \frac{1-\cos\theta}{1+q^2 r_{c1}^2} + \frac{1+\cos\theta}{1+q^2 r_{c3}^2} \right).$$

The correlation radii  $r_{c1}$ ,  $r_{c2}$ , and  $r_{c3}$  have the same temperature dependences and they are related by

$$4r_{c3}^2 = r_{c1}^2 + 3r_{c2}^2.$$

If the intensity of the scattered light is integrated over all the directions, the following expression is obtained for the extinction coefficient:

$$\sigma = \pi R_{sc} (\varphi_1 + \varphi_2 + \varphi_3), \quad (3)$$

where

$$\varphi_1 = \frac{1}{4\beta_1^2} \left[ \frac{4\beta_1^2 - 4\beta_1 + 1}{2\beta_1} \ln(1+2\beta_1) - 1 + 5\beta_1 \right],$$

$$\varphi_2 = \frac{1}{12\beta_2^2} \left[ \frac{20\beta_2^2 + 8\beta_2 + 1}{2\beta_2} \ln(1+2\beta_2) - 1 - 7\beta_2 \right], \quad (4)$$

$$\varphi_3 = \frac{1}{\beta_3^2} \left[ \frac{2\beta_3 + 1}{2} \ln(1+2\beta_3) - \beta_3 \right],$$

$$\beta_i = 2(kr_{ci})^2, \quad i=1, 2, 3.$$

Throughout the investigated range of temperatures, within the limits of the experimental error, we found no angular dependence of the scattered-light intensity. Therefore, we shall use the expressions for the intensity of the scattered light and the extinction coefficient in the  $kr_{ci} = 0$  approximation. In this case Eq. (3) becomes

$$\sigma = (40\pi/9) R_{sc}. \quad (5)$$

Multiple scattering of light was allowed by us in the same way as in Refs. 11 and 12, i.e., measurements were made of the intensity when the illuminated volume  $V_1$  and the volume  $V_2$  from which light was received by the recording device were separated from one another by a distance  $h$ . In the case when the volumes  $V_1$  and  $V_2$  were thin cylinders of length  $2L_0$  and cross sections  $s_1$  and  $s_2$ , the intensity of the doubly scattered light for a tensor order parameter and a cell of cylindrical shape could be described by

$$I_\beta^{\alpha(2)} = \frac{I_0}{R^2} R_{sc}^2 s_1 s_2 \int_{-L_0/h}^{L_0/h} dl_1 \int_{-L_0/h}^{L_0/h} dl_2 \frac{\Gamma_\beta^\alpha}{l^2+1}, \quad h \neq 0, \quad (6)$$

where

$$\Gamma_z^z = \frac{1}{36} \left[ 25 - \frac{8}{l^2+1} + \frac{1}{(l^2+1)^2} \right],$$

$$\Gamma_{xy}^z = \frac{1}{3} \left[ 2 - \frac{1+l_1^2 \sin^2 \theta}{4(l^2+1)} + \frac{l_1^2 \sin^2 \theta}{12(l^2+1)^2} \right],$$

$$\Gamma_{xy}^y = \frac{1}{36} \left[ 24 + \cos^2 \theta - 3 \sin^2 \theta \frac{l_1^2 + l_2^2}{l^2+1} - \frac{l_1 l_2 \sin \theta \sin 2\theta}{l^2+1} + \frac{l_1^2 l_2^2 \sin^4 \theta}{(l^2+1)^2} \right],$$

$$l^2 = l_1^2 + l_2^2 - 2l_1 l_2 \cos \theta.$$

In the derivation of Eq. (6) we have allowed for the fact that the difference between the paths traversed by singly and doubly scattered light is small compared with the attenu-

ation length  $\sigma^{-1}$ . In the case of  $h = 0$  we find that, to within a logarithmic accuracy in respect of the small parameter  $r_M/L_0$ ,

$$I_z^{z(2)} = \frac{I_0}{R^2} R_{sc}^2 s_1 s_2 \ln \frac{L_0}{r_M}, \quad (7)$$

where  $r_M$  is the radius of the larger of the two cylinders.

## 2. EXPERIMENTAL RESULTS

Measurements were made using apparatus described in Ref. 11. An He-Ne laser was used as the source of light. The precision of the measurements was improved by determining the intensities of the scattered and transmitted light in units of the incident-light intensity. A cylindrical cell containing the investigated liquid crystal had a diameter of  $2L_0 = 3$  cm

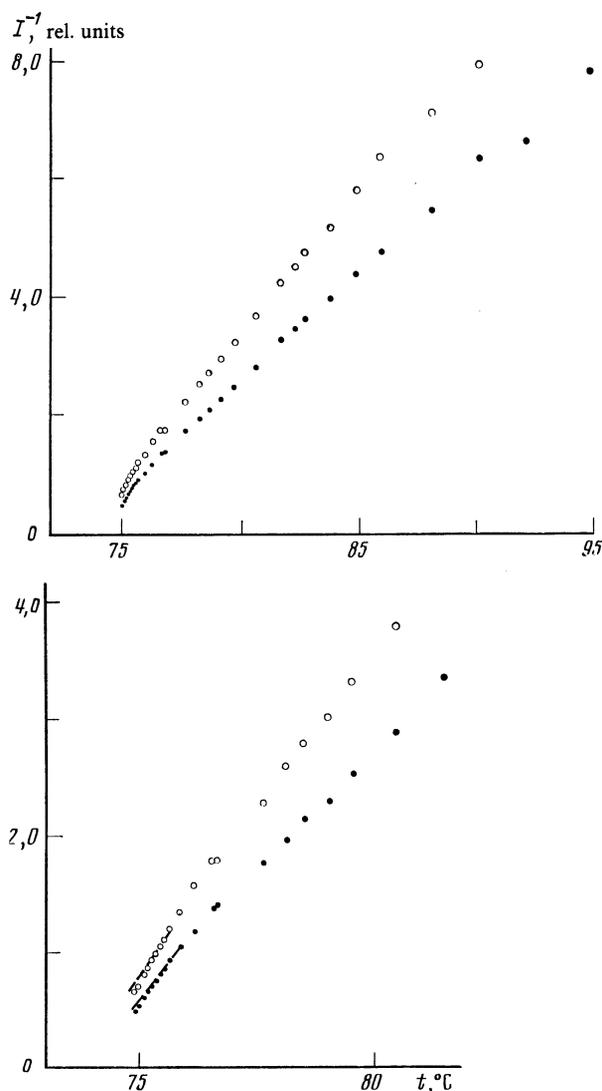


FIG. 1. Temperature dependences of the scattered-light intensity obtained for  $\theta = \pi/2$ ; (●)  $I_z^z$  component; (○)  $I_z^x$  component; the results of subtraction of the contribution of the double scattering is shown on an enlarged scale (by the dashed curves) on the right.

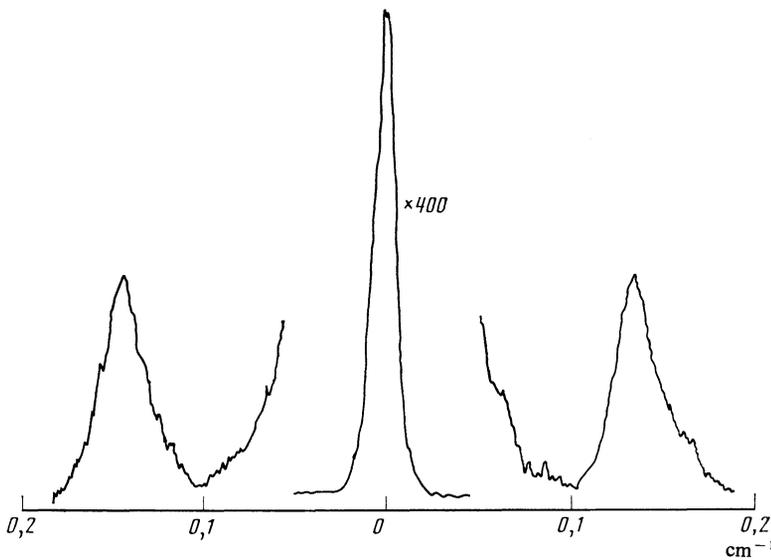


FIG. 2. Spectral composition of the scattered-light component  $I_z^z$  at  $t = 86^\circ\text{C}$  for  $\theta = \pi/2$ .

and it was enclosed in a massive copper jacket, which was thermostated to within  $\sim 0.005^\circ\text{C}$ . The temperature dependences of the intensities  $I_z^z$  and  $I_{xy}^z$  of the scattered light are plotted in Fig. 1 for the scattering angle  $\theta = \pi/2$ .

The intensity  $I_z^z$  of the scattered light includes contributions not only from fluctuations of the order parameter, but also from fluctuations of the density. An estimate of the contribution of these fluctuations was obtained by investigating the scattered-light spectrum (Fig. 2) obtained using a three-pass Fabry-Perot interferometer stabilized by a DAS-1 system. It is clear from Fig. 1 that the integrated contribution of the scattering by fluctuations of the density did not exceed 2%.

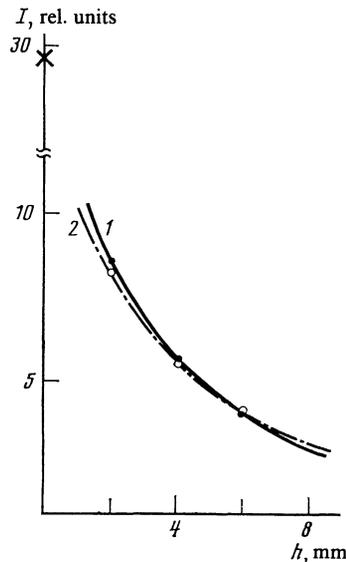


FIG. 3. Dependence of the intensity of the doubly scattered light on the distance  $h$  between the illuminated and investigated regions. The theoretical curves are calculated using Eq. (6): 1)  $I_z^{(2)}$  component; 2)  $I_x^{(2)}$ . The experimental values of these components are denoted by  $\bullet$  and  $\circ$ , respectively; here, the symbol  $\times$  denotes  $I_z^{(2)}(h=0)$  at  $t = 75.2^\circ\text{C}$ .

We measured the  $I_z^z$  and  $I_x^z$  components of the multiply scattered light for  $\theta = \pi/2$ . The results of a comparison of the experimental and calculated [from Eq. (6)] values of the intensity is made in Fig. 3. The good agreement between the theory and experiment shows that only single and double scattering need be allowed for. It should be pointed out that, in contrast to the case of a scalar order parameter,<sup>11,13</sup> the polarized and depolarized components of the scattered light increase strongly in the limit  $h \rightarrow 0$  and the depolarization coefficient of doubly scattered light is close to 1, instead of 3/4 for singly scattered light.

The doubly scattered light was subtracted from the total intensity corresponding to  $h = 0$  with a logarithmic accuracy by the application of Eq. (7). Its contribution did not exceed 3%. The intensity of the singly scattered light alone is plotted in Fig. 1. We can see that the deviation from the universal temperature dependence of the scattered-light intensity cannot be explained by multiple scattering. Throughout the investigated range of temperatures the depolarization coefficient is 3/4.

The optical properties of a scattering system are governed by the absolute value of the scattering constant  $R_{sc}$ . Usually the value of  $R_{sc}$  is found by comparing the scattered-light intensity with the intensity of light scattered by a standard system kept under the same experimental conditions. In our case this task is greatly simplified by the strong temperature dependences of the intensities of the scattered and transmitted light and the absence of the scattering asymmetry. The intensities of the transmitted  $I_{tr}$  and the scattered  $I_{sc}$  light after subtraction of the contribution of the double scattering can be written in the form

$$I_{tr} = I_{tr}^0 \exp\left(-\frac{40\pi}{9} R_{sc} \cdot 2L_0\right), \quad (8)$$

$$I_{sc}/I_{tr} = \Lambda^0 R_{sc}, \quad (9)$$

which gives

$$\ln I_{tr} = \ln I_{tr}^0 - \frac{80\pi L_0}{9} \frac{I_{sc}}{I_{tr} \Lambda^0} \quad (10)$$

TABLE I. Temperature dependence of light-scattering constant of BMOAB in isotropic phase ( $\lambda = 6328 \text{ \AA}$ )

| $t, ^\circ\text{C}$ | $R_{sc} \cdot 10^3, \text{cm}^{-1}$ | $t, ^\circ\text{C}$ | $R_{sc} \cdot 10^3, \text{cm}^{-1}$ | $t, ^\circ\text{C}$ | $R_{sc} \cdot 10^3, \text{cm}^{-1}$ |
|---------------------|-------------------------------------|---------------------|-------------------------------------|---------------------|-------------------------------------|
| 94,75               | 1,07                                | 79,65               | 3,40                                | 75,52               | 9,87                                |
| 89,95               | 1,25                                | 79,15               | 3,74                                | 75,43               | 10,17                               |
| 88,0                | 1,53                                | 78,6                | 3,98                                | 75,33               | 11,00                               |
| 85,8                | 1,76                                | 78,2                | 4,32                                | 75,28               | 11,70                               |
| 84,8                | 1,91                                | 77,6                | 4,88                                | 75,185              | 12,59                               |
| 83,7                | 2,12                                | 76,7                | 6,14                                | 75,085              | 13,65                               |
| 82,6                | 2,30                                | 76,65               | 6,15                                | 74,95               | 15,64                               |
| 82,2                | 2,43                                | 76,2                | 7,19                                | 74,885              | 16,92                               |
| 81,65               | 2,56                                | 75,9                | 8,09                                |                     |                                     |
| 80,6                | 2,97                                | 75,65               | 9,09                                |                     |                                     |

at any temperature. Equation (10) was fitted as closely as possible to the experimental results and this gave the parameters  $I_{tr}^0$  and  $A^0$ , which were then used to find the temperature dependence of the scattering constant  $R_{sc}(T)$ . The values of this constant are listed in Table I.

An analysis of the temperature dependence of the ratio  $T/R_{sc}$  showed that in the interval of temperatures defined by  $t = T - 273.16^\circ\text{C}$  extending from 95 to  $76^\circ\text{C}$  it can be described by the relationship

$$T/R_{sc} = A(T - T^*) \quad (11)$$

(where  $A = 1.61 \times 10^4 \text{ cm}$ ,  $T^* = t^* + 273.16^\circ\text{C}$ ,  $t^* = 73.20^\circ\text{C}$ ) with an error not exceeding 1%, which corresponds to the *a priori* expected precision of the intensity measurements. The temperature of the discontinuity at the first-order phase transition  $t_c$  is  $74.80\text{--}74.85^\circ\text{C}$ . The precision of the approximation deteriorated when points corresponding to  $t < 76^\circ\text{C}$  were included in the analysis.

### 3. ANALYSIS OF EXPERIMENTAL RESULTS

The isotropic phase-nematic liquid crystal (*I-N*) phase transition is usually described by the effective Hamiltonian  $H$  using the Landau-de Gennes model.<sup>10,14,15</sup>

$$H = \int d\tau [^{1/2}a\tau \text{Sp } \hat{s}^2 - ^{1/2}L_1 \text{Sp } (\hat{s} \Delta \hat{s}) + ^{1/2}L_2 \text{Sp } (\nabla \hat{s})^2 - ^{1/3}B \text{Sp } \hat{s}^3 + ^{1/4}C (\text{Sp } \hat{s}^2)^2 + ^{1/5}E \text{Sp } \hat{s}^2 \text{Sp } \hat{s}^3 + ^{1/6}D_1 (\text{Sp } \hat{s}^2)^3 + ^{1/6}D_2 (\text{Sp } \hat{s}^3)^2], \quad (12)$$

where  $\tau = (T - T^*)/T^*$ . The presence of a large rectilinear section in the temperature dependence of the reciprocal of the scattered-light intensity suggests that in this case the role of nonlinear terms is relatively small so that we can use perturbation theory, which is in contrast to the usual situation. The correction terms may be responsible for the deviation from linearity near the transition point.<sup>3</sup> It follows from Eqs. (2) and (12) that  $R_{sc}$  can be described by

$$R_{sc} = \frac{\pi^2 k_B T}{\lambda^4 g(\tau)}, \quad (13)$$

where

$$g(\tau) = a\tau \{ 1 - y_C \tau^{-1/2} - y_B \tau^{-3/2} + y_D - [^{1/7}y_C^2 - y_{BE}] \tau^{-1} \ln \tau^{-1} - ^{25/63}y_B^2 \tau^{-3} + ^{3/11}y_C y_B \tau^{-2} \}. \quad (14)$$

Here,

$$y_C = 7M \frac{c}{a}, \quad y_B = \frac{7}{16} M \frac{B^2}{a^2}, \quad y_D = \frac{7}{2} M^2 \frac{18D_1 + D_2}{a},$$

$$y_{BE} = \frac{77}{150} M^2 \frac{BE}{a^2}, \quad M = \frac{k_B T^*}{4\pi a r_0^3}.$$

Equation (14) is obtained in the approximation of one correlation length  $r_c = r_0 \tau^{-1/2} (L_2 = 0)$ . It allows for two-loop diagrams determined with a logarithmic precision with respect to  $\tau$ . Within the framework of this approximation the fifth- and sixth-order terms contribute only to the two-loop diagrams. The range of validity of the expansion (14) is governed by the conditions

$$y_C \tau^{-1/2} \ll 1, \quad y_B \tau^{-3/2} \ll 1, \quad y_D \ll 1,$$

$$y_{BE} \tau^{-1} \ln \tau^{-1} \ll 1,$$

which in this case act as the Ginzburg criterion.

An initial analysis of the experimental results was carried out ignoring the fifth- and sixth-order terms ( $y_D = 0$ ,  $y_{BE} = 0$ ). Formulas (13) and (14) then described—with the *a priori* expected experimental precision—the temperature dependence  $R_{sc}(T)$  throughout the investigated range. The parameters  $a$ ,  $T^*$ ,  $y_C$ , and  $y_B$  could also be determined. The value of  $a$  could be found more reliably than that of the others and this parameter governed mainly the slope of the temperature dependence of  $R_{sc}^{-1}$  in Eq. (11):  $a = 39 \pm 2 \text{ J/cm}^3$ . The value of  $y_C$  was subject to the greatest error and it was found to lie within the range  $-0.08 < y_C < -0.02$ . The range of permissible values of the parameters  $y_B$  and  $T^*$  for a

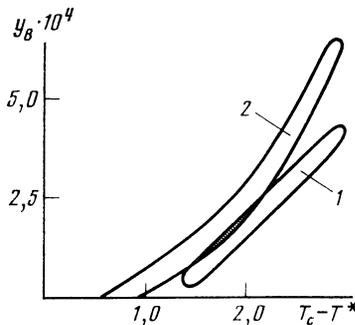


FIG. 4. Ranges of permissible values of  $T^*$  and  $y_B$ : 1) light-scattering experiments; 2) measurements of the specific heat. The shaded region is shared by both cases.

fixed value  $y_C = -0.03$  is plotted in Fig. 4.

The experimental data on the specific heat of the isotropic phase of BMOAB were analyzed in a similar manner.<sup>6</sup> The calculation of  $C_p$  in the model of Eq. (12) with the same relative precision as that in the derivation of Eq. (14) (including diagrams with up to three loops) gave

$$C_p = X + Y\tau + \frac{5k_B\tau^{-1/2}}{16\pi r_0^3} \left\{ 1 + \frac{2}{3} y_B \tau^{-1/2} + 0.8 y_B^2 \tau^{-3} + \frac{1}{2} y_D + 0.06 y_B y_C \tau^{-2} + \frac{1}{2} \left[ \frac{1}{7} y_C^2 - y_{BE} \right] \tau^{-1} \ln \tau^{-1} \right\}, \quad (15)$$

where  $X$  and  $Y$  describe the regular part of the specific heat. The coefficient in front of  $y_B^2$  is subject to an error not exceeding 10% and this error is due to the difficulties encountered in estimating of one of the integrals which occur in the expression for this parameter.

An analysis of the experimental data on the basis of Eq. (15) with  $y_{BE} = 0$  and  $y_D = 0$ , carried out in the range  $1^\circ\text{C} \leq T - T_c \leq 20^\circ\text{C}$  gave stable values of  $r_0$  within the limits  $5.5\text{--}6.5 \text{ \AA}$ . It should be pointed out that the value of  $r_0$  for MBBA is located in the same range of temperatures: this value was deduced in Ref. 2 from precision measurements of the scattered-light indicatrix. The value of  $y_C$  was determined less accurately than from the scattered-light data:  $-0.1 < y_C < 0$ . It is worth noting (Fig. 4) that the specific-heat data yield a higher value of  $y_B$  than the optical data. This is clearly due to the fact that the higher terms of the expansion for the specific heat are of greater relative weight, as is clear from Eqs. (14) and (15). For the same reason of a greater weight of the terms which are dropped, it is found that Eq. (15) does not describe the specific heat with the *a priori* expected experimental accuracy in the temperature range  $0^\circ\text{C} < T - T_c < 1^\circ\text{C}$ .

The negative value of the coefficient  $C$  demonstrates the need to include in (12) the terms up to the sixth order in order to ensure stability of the system. However, we can see from Eqs. (14) and (15) that the sixth-order term  $y_D$  results mainly in refinement of the expansion coefficients  $a$ ,  $y_B$ , and  $y_C$ , because  $y_D$  is independent of temperature. The influence of the fifth-order term is clearly not very great, because it occurs only in the second-order corrections.

Unfortunately, the precision of the available experimental data above the transition point is insufficient for the determination of  $y_D$  and  $y_{BE}$ . We estimated these coefficients using the experimental temperature dependence of the order parameter<sup>7</sup> of the nematic ( $N$ ) phase. In the case of a uniaxial nematic liquid crystal the equilibrium value of the order parameters is

$$S_{\alpha\beta}^0 = \varepsilon_\alpha (n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta}), \quad (16)$$

where  $\varepsilon_\alpha = \varepsilon_{\parallel} - \varepsilon_{\perp}$ ;  $\mathbf{n}$  is the director vector;  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$  are the permittivities along and across  $\mathbf{n}$ . If we allow for Eqs. (12) and (16), we find that the contribution to the thermodynamic potential of the  $N$  phase associated with the order parameter is given by the following expression if no allowance is made for the fluctuation corrections:

$$\Phi = \frac{1}{3} a \tau \varepsilon_\alpha^2 - \frac{2}{27} B \varepsilon_\alpha^3 + \frac{1}{9} C \varepsilon_\alpha^4 + \frac{4}{135} E \varepsilon_\alpha^5 + \frac{1}{6} D \varepsilon_\alpha^6, \quad (17)$$

where  $D = (4/81)(6D_1 + D_2)$ .

The condition for the minimum of the thermodynamic potential of Eq. (17) is given by the following equation which describes the temperature dependence of  $\varepsilon_\alpha$ :

$$\frac{2}{3} a \tau - \frac{2}{9} B \varepsilon_\alpha + \frac{4}{9} C \varepsilon_\alpha^2 + \frac{4}{27} E \varepsilon_\alpha^3 + D \varepsilon_\alpha^4 = 0. \quad (18)$$

The experimental data on the temperature dependence of  $\varepsilon_\alpha$  were deduced from the measured<sup>7</sup> values of the differences between the refractive indices of the ordinary and extraordinary rays ( $\lambda = 6328 \text{ \AA}$ ) in the temperature interval  $T_c - T \approx 50^\circ\text{C}$ . The indeterminacy in the value of the coefficients was reduced by applying additionally the equality of the thermodynamic potentials in isotropic and nematic phases at the phase transition point:

$$a \tau_\varepsilon - \frac{2}{9} B \varepsilon_c + \frac{1}{3} C \varepsilon_c^2 + \frac{4}{45} E \varepsilon_c^3 + \frac{1}{2} D \varepsilon_c^4 = 0, \quad (19)$$

where  $\varepsilon_c = (T_c - T^*)/T^*$  and  $\varepsilon_c = \varepsilon_\alpha(T_c)$ .

In the temperature interval  $4^\circ\text{C} \leq T_c - T \leq 50^\circ\text{C}$  Eq. (18) describes the experimental results to within 0.2%. Closer to the transition point we can achieve the same experimental accuracy only if we allow for the fluctuation corrections, exactly as in the isotropic phase case. For the same reason the condition (19) can be regarded only as an estimate.

The parameter  $D/a$  has the value  $0.14 \pm 0.02$  and is found to be weakly correlated with the other parameters of the system. This reflects the important role of the sixth-order term in the description of the dependence  $\varepsilon_\alpha(T)$ . For example, an attempt to exclude this term from the description (by postulating  $D = 0$ ) results in a serious deterioration of the agreement with the experimental results even if terms of higher orders are included in Eq. (18). An analysis also shows that the parameters  $B$ ,  $C$ , and  $E$  are strongly correlated and suffer from large errors. We can simply say that for a liquid crystal under investigation the  $N$  phase is characterized by  $C < 0$  and  $E > 0$ . A more accurate determination of the coefficients of the  $N$  phase requires in an allowance for the results of other experiments, particularly those on the temperature dependence of the specific heat, but in this case (as for  $\varepsilon_\alpha$ ) we have to allow for the fluctuation corrections.

The value of  $D/a$  obtained in this way was used to estimate the correction to the coefficient  $a$  for the  $I$  phase. For  $D_2 = 0$ , the coefficient  $a$  decreased by about 5%. The influence of the sixth-order term on the value of  $r_0$  was also slight. An allowance for the cross term  $y_{BE}$  reduced somewhat the contribution of the logarithmic term in Eqs. (14) and (15), which affected mainly the numerical value of  $y_C$ , but did not alter the conclusion that  $y_C < 0$ .

It follows that the model corresponding to Eq. (12) allows us to describe the temperature dependence of the scattered-light intensity and of the specific heat of the isotropic phase of the investigated material. The extreme critical behavior corresponding to the fluctuation region is not observed although the fluctuation corrections at the transition point are very large (particularly in the case of the specific heat). The distinguishing features of the model (12) are the negative value of the coefficient  $C$ , obtained in the experi-

ments considered by us, and the need to allow for the sixth-order term.

The authors regard it as their pleasant duty to thank M. A. Anisimov for discussing the results.

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