

Optically induced impurities in the two-phase region of a liquid crystal

Yu. A. Reznikov, V. Yu. Reshetkin, and S. V. Yaroshchuk

Physics Institute, Ukrainian Academy of Sciences

(Submitted 23 October 1991)

Zh. Eksp. Teor. Fiz. **101**, 1529–1540 (May 1992)

Nematic liquid crystal samples that are homogeneous in the region of coexistence of the nematic and isotropic phases were obtained and used, for the first time ever, for experimental investigation of the optical nonlinearity due to phototransformation of molecules. It is shown that the nonlinear phase shift in the course of photoisomerization and of molecules by optically induced heating is due to changes of the refractive indices of the coexisting phases as well as to a redistribution of their volumes. The results are explained in the framework of a qualitative model that interprets the optical action on the medium in the two-phase region as a shift of the operating point on the temperature vs density diagram of the impurity.

The long-range orientational order of the arrangement of molecules in liquid crystals makes them uniquely sensitive to light. Particularly strong are effects of reversible optically induced changes of the refractive index, which are phenomenologically described by the cubic term of the expansion of the liquid-crystal polarization in powers of the light-field intensity E (cubic nonlinearity).¹

One of the types of cubic optical nonlinearity of nematic liquid crystals (NLC), actively studied of late, is the so-called conformational nonlinearity.² The refractive-index change corresponding to this nonlinearity is determined by the change of the polarizability of the molecules as they are photoconverted and by the change of the order parameter s of the NLC near these molecules. A change of s leads to giant values of the conformational-nonlinearity parameter $\varepsilon_2 = 2n\Delta n/E^2$ of the mesophase.

Since the change of the order parameter by the light and its contribution to the value of Δn increase drastically as the temperature T_c of the transition into the isotropic phase is approached, the nonlinearity is particularly large near T_c (Refs. 3 and 4). However, investigations and applications of nonlinear-optics effects near a phase transition (PT) entail a number of complicating factors, principal among which are the need for precise temperature stabilization, narrow dynamic ranges of the temperature stabilization, and also linearity of the variation of the refractive index with the light intensity and strong heterogeneity of the system in the phase-transition (PT) region, when the system breaks up into drops of the nematic and isotropic phases.

These difficulties can be overcome to a significant degree by expanding the PT region, ensuring thereby a sufficient optical homogeneity of the system. This possibility was afforded by introducing into the NLC various impurities, for in this case the PT temperature range is broadened and a sufficiently wide temperature region is produced in which the nematic (NP) and isotropic (IP) phases coexist (two-phase region).⁵

As shown in Refs. 5–8, the temperatures of the transitions from the nematic state into the two-phase region (T_n) and from the two-phase region into the isotropic phase (T_i) decrease linearly under typical experimental conditions with increase of the overall impurity density c' :

$$T_{n,i} = T_{c0}(1 - \alpha_{n,i} c') \quad (1)$$

(T_{c0} is the PT temperature of pure NLC, $\alpha_{n,i}$ are propor-

tionality coefficients, $\alpha_n > \alpha_i$), i.e., the width of the two-phase region is proportional to c' (Fig. 1). The ratio of the volumes V_n (NP) and V_i (IP) in the regions of their existence, corresponding to the equilibrium impurity densities c'_n and c'_i , is determined by the known lever rule (see Fig. 1)

$$\frac{V_n}{V_i} = \frac{c'_i - c'}{c' - c'_n} \quad (2)$$

In addition, as shown in Ref. 8, the variations of $c'_{n,i}$ and of the order parameter s of the NP are independent of the total impurity density c' and are determined by the intermolecular-interaction parameters. The temperature dependence of s is usually weak. In typical situations the order of magnitude of the relative changes $\Delta s/s$ in the entire range of existence of the mesophase are of the order of 10^{-2} .

In the usual experimental situations the two-phase region is an optically inhomogeneous medium consisting of randomly located regions of isotropic and nematic phases. However, as shown in Refs. 9–10, in a number of cases there can be formed also optically quite homogeneous layered structure of the IP–NP–IP type, which can be conveniently investigated by the methods of linear and nonlinear optics. In particular, in the NLC MBBA, which is homeotropically ordered in the mesophase and whose phase-transition temperature is lowered by its temperature degradation, transitions into IP are possible through the two-phase region whose structure, while containing a number of defects (disclinations, point defects) is sufficiently homogeneous for optical measurements.

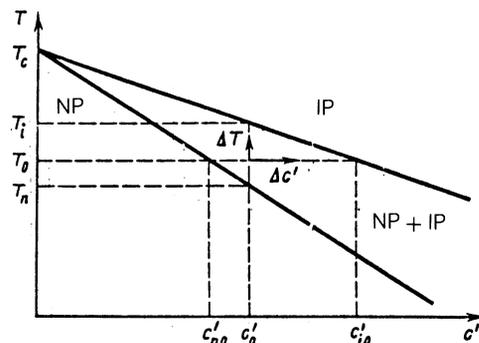


FIG. 1. Phase diagram of impurity NLC. The values of ΔT and $\Delta c'$ determine the shift of the operating point (c'_0, T_0) of NLC heating and for excitation of optically induced impurities, respectively.

We report here a first investigation of the cubic optical nonlinearity of NLC in the NP and IP coexistence region produced by photoisomerization of the liquid-crystal molecules and by optical heating. In the first part we describe the method of preparing the sample and its properties. In the second we report the experimental results, which are described in the third part in the context of a qualitative model proposed for nonlinearity in the two-phase region.

1. LAYERED STRUCTURE OF IMPURITY NLC IN THE TWO-PHASE REGION

As indicated in the Introduction, an impurity NLC should constitute a unique nonlinear-optics system if it is produced in such a way that a two-phase region exists in a wide temperature interval and is sufficiently homogeneous. It is also desirable that the director orientation in the NP be predominantly planar, for in this case the cubic optical nonlinearity can reach maximum values.²⁻⁴

To obtain such systems we tested a number of NLC with various impurities,⁸ but the only one satisfying the above requirements was the NLC MBBA, with planar orientation in the mesophase and with natural impurities (products of its degradation). The sample was made by pouring nominally pure MBBA ($T_{co} = 43^\circ\text{C}$) in a normal atmosphere into a cell made of glass slabs. Water interacts with the NLC to produce irreversible decomposition with formation of parasubstituted benzaldehyde and aniline, which in turn oxidized.¹¹ This degradation of the NLC led to a lowering of the temperature T_c and to the appearance of a two-phase region about 2 deg. wide ($T_n = 26^\circ\text{C}$).

A rough estimate of the total impurity density in the sample, by comparison with the experimental results for the phase MBBA-benzaldehyde diagram,¹³ yields a value $c' \approx 10^{-1}$ for the impurity density. Since the impurity density is low, it can be assumed that T_n and T_i decrease linearly with increase of c' (1) up to the obtained value of c' . Taking into account the value $T_{co} = 43^\circ\text{C}$ and also recognizing that $T_{co} = 43^\circ\text{C}$, $T_n = 26^\circ\text{C}$ and $T_i = 28^\circ\text{C}$ we obtain from (1) that $\alpha_n = 0.54$, $\alpha_i = 0.48$.

To obtain a homogeneous structure, the sample was heated adiabatically starting with room temperature (heating rate 10^{-2} deg/min. After entering in the two-phase region, a quite homogeneous optically anisotropic structure (the defect-free regions amounted to 2–5 cm²). An analysis of the textures⁸ has shown that this structure constitutes a sandwich of an NP between two IP wall layers (Fig. 2).

The causes of this sandwich may be the good, compared with the mesophase, wetting of the IP surface of the orientant, and also the increased densities of water molecules and impurities on its surface.¹³ The orientation \mathbf{n} of the director in the NP layer was close to the \mathbf{n} direction in the mesophase.

The relatively good quality of the obtained system

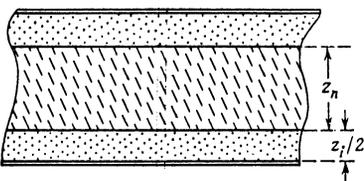


FIG. 2. Phase structure of NLC in a two-phase region.

makes it useful not only for the investigation of nonlinear-optics effects but also for the use of relatively simple linear-optics methods to verify the validity of the results of the preceding part of the work. To this end, we measured the temperature dependences of the phase difference φ_a between the o - and e -waves on passing through the sandwich.

A testing light beam of an Ne-He laser ($\lambda_l = 0.63 \mu\text{m}$) with a wave vector perpendicular to the director and a vector E_l making an angle 45° with \mathbf{n} was directed into the cell at $T < T_n$. A polarizer with a transmission axis perpendicular to the polarization of E_l was mounted past the cell. Its output intensity I_l^{out} was connected with the NP birefringence and with the NP thickness z_n by the relation

$$I_l^{\text{out}} = I_l \sin^2 \varphi_a, \quad \varphi_a = \frac{2\pi}{\lambda} n_a z_n, \quad n_a = n^e - n^o,$$

where n^o and n^e are the refractive indices for the o - and e -waves. The low testing-radiation intensity $I_l \approx 0.01 \text{ W/cm}^2$ made it possible to exclude completely the possible influence of orientational and other types of linearity on the experimental results. The results are shown in Fig. 3. The value of φ_a shows a jump at the point T_n , followed by a linear, within the limits of experimental error, decrease of φ_a all the way to the point T_i , where φ_a vanishes.

We explain the results using the expression for φ_a . According to Ref. 14, the relations for $n^{o,e}$ and n_a of an impurity NLC are of the form

$$(n^{o,e})^2 = 1 + \frac{4\pi h F}{V_n} (N_n + N_n') (\bar{\gamma} + g \bar{\gamma}_a s), \quad (3)$$

$$n_a = \frac{4\pi h F \bar{\gamma}_a s}{(n^o + n^e) V_n} (N_n + N_n'), \quad (4)$$

where N_n and N_n' are, respectively, the numbers of the proper and impurity molecules in the NP, V is the NP volume, $\bar{\gamma} = (1 - c_n')\gamma + c_n'\gamma'$, γ and γ' are the polarizabilities of the matrix and impurity molecules, γ_a and γ'_a are the anisotropies of these polarizabilities, $\bar{\gamma}_a = (1 - c_n')\gamma_a + c_n'\gamma'_a$, $g = -1/3$ for the o -waves and $g = 2/3$ for the e -wave, and F and h are local-field factors.

The expression for the nematic-layer thickness follows from the lever rule (2) and relations (1)

$$z_n = L T_{co} \left(\frac{1}{T_{co} \alpha_i} - \frac{1}{T_{co} - T} \right) / \left(\frac{1}{\alpha_i} - \frac{1}{\alpha_n} \right) \quad (5)$$

(L is the cell thickness, i.e., $L = z_i + z_n$).

Since $c_{n,i} \ll 1$ in our case, it can be seen from (5) that

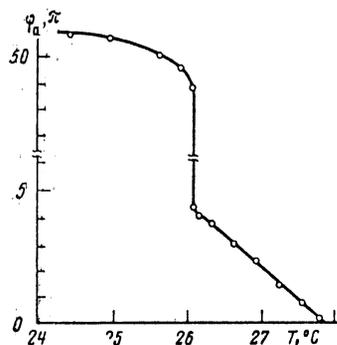


FIG. 3. Temperature dependence of φ_a .

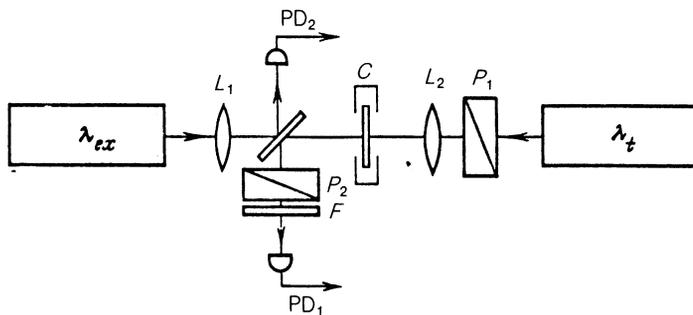


FIG. 4. Diagram of experimental setup: L_1 - L_2 —lenses, F —red filter, P_1 - P_2 —polarizers, PD_1 - PD_2 —photodiodes, C —cell with NLC.

after going through the point T_n the thickness of the nematic layer should decrease linearly with temperature owing to the decrease of the NP layers, and $z_n = 0$ at $T = T_i$.

Compared with so strong a temperature dependence of $z_n(T)$, the temperature dependence of $n_a(T)$ should be considerably weaker. In fact, it is reasonable to assume that the molecular parameters γ , γ' , γ_a , and γ'_a , the local-field coefficients F and h , and the value of $(N_n + N'_n)/V_n$ in the region of the phase existence are practically independent of temperature. The change of c'_n in the range of the two-phase region is $[c'_n(T \rightarrow T_n) - c'_n(T \rightarrow T_i)]/c'_n(T \rightarrow T_n) \approx 0.1$ for the two-phase region parameters realized in our case. The $c'_n(T)$ dependence can therefore also be neglected compared with the strong $z_n(T)$ dependence. As indicated in the Introduction, the variation of s in NP of the two-phase region is also extremely small and the $s(T)$ dependence can be neglected.

Thus, φ_a decreases practically linearly with temperature, owing to the decrease of the NP layer. The obtained experimental $\varphi_a(T)$ dependence exhibits just such a behavior. However, the value of φ_a as $T \rightarrow T_n$ on the side of the two-phase region is not equal to the value as $T \rightarrow T_n$ on the side of the two-phase region, as follows from the theory, but is substantially smaller—it undergoes a jump on going entering the two-phase region. This jump can be explained by recognizing that the direction of the director of MBBA on the boundary with the isotropic phase differs from the initial planar orientation established in the transition, and makes an angle 27°C with the boundary.¹⁰ The reason for the jump of φ_a is therefore that at the point $T = T_n$ there is produced on the orientant surface a thin IP film. Estimates in Ref. 8 show that the φ_a jump on entering the two-phase region corresponds to a change of φ_a on account of reorientation of \mathbf{n} by an angle of the order of 30° from planar.

Thus, quasi-adiabatic heating of the NLC MBBA plane-polarized in the mesophase and produces near the orienting surfaces, after reaching a temperature T_n , an IP layer whose director orientation on the boundary differs from that on the NLC orientant boundary. With further rise of temperature the thickness of the NP, whose order parameter is practically invariant, decreases linearly. When the temperature T_i is reached the specimen becomes fully isotropic.

2. EXPERIMENTAL RESULTS

We investigated experimentally the optically induced change of the phase difference between e - and o -waves passing through the sample. The sample characteristics were indicated above. The experimental setup is shown in Fig. 4.

The Gaussian beams, one exciting ($\lambda_{ex} = 0.44 \mu\text{m}$, power $P_{ex} = 5 \text{ mW}$) and the other testing ($\lambda_t = 0.63 \mu\text{m}$, $P_t = 0.1 \text{ mW}$), intersected in the sample. The radius of the exciting beam ($\rho_{ex} = 0.6 \text{ mm}$) was much larger than the radius of the testing beam ($\rho_t = 0.2 \text{ mm}$), made it possible to regard the intensity I_{ex} as constant in the region of their intersection.

The wave vectors of both beams were perpendicular to the director \mathbf{n} of the NLC in the mesophase. The polarization of the testing radiation \mathbf{E}_t made was at 45° to \mathbf{n} , and the polarization of \mathbf{E}_x was parallel to \mathbf{n} . The testing beam passed from the sample through a polarizer with an axis perpendicular to \mathbf{n} and was recorded by photodiode PD_1 . The power of the exciting was monitored by photodiode PD_2 . The sample temperature was set to minimize the power of the testing radiation past the polarizer, i.e., to satisfy the condition $\varphi_a = m\pi$, $m = 1, 2, \dots$.

The exciting-light wavelength was at the MBBA absorption edge (absorption coefficient $\beta = 13 \text{ cm}^{-1}$). Absorption of light caused photoionization of the MBBA molecules and heating of the crystal.^{15,16} As a result, pulsed application of the exciting beam altered the phase shift φ_a , and the photodiode PD_1 connected to an automatic plotter recorded a signal proportional to $I_t \sin^2[\Delta\varphi_a(I_{ex} = \text{const})]$.

The results of measuring the stationary variation of $\Delta\varphi_a^s$ as a function of the light intensity in the middle of the two-phase region were poorly reproducible. Its character in this region was qualitatively the following. On the initial section the value of $\Delta\varphi_a^s$ increased linearly with the intensity I_{ex} , but with further increase of I_{ex} ($I_{ex} \gtrsim 0.8 \text{ W/cm}^2$) the increase of $\Delta\varphi_a$ became faster than linear. At still larger I_{ex} ($\approx \text{W/cm}^2$) the stationary value of $\Delta\varphi_a$ decreased past a

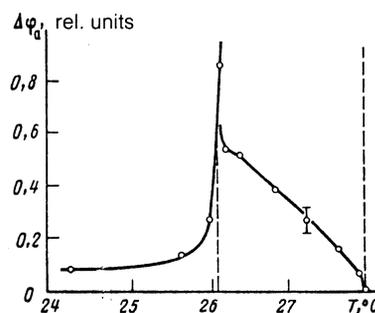


FIG. 5. Temperature dependence of the stationary nonlinear phase shift $\Delta\varphi_a$ ($I_{ex} = 0.05 \text{ W/cm}^2$).

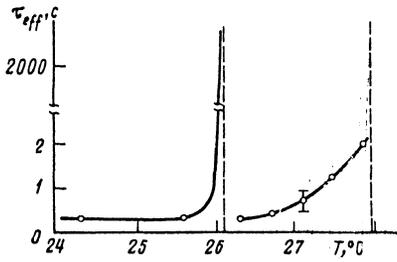


FIG. 6. Temperature dependence of the effective time τ_{eff} of nonlinear phase-shift relaxation.

certain threshold to zero. The onset of this state was accompanied by intense scattering of light.

We obtained also the temperature dependences of $\Delta\varphi_a^s(T)$ (Fig. 5) and of the effective relaxation time τ_{eff} of $\Delta\varphi_a$ (Fig. 6). This time corresponds to a decrease of $\Delta\varphi_a(t)$ by e times. Critical growth of $\Delta\varphi_a^s$ and τ_{eff} was observed in the vicinity of the temperature T_n in the mesophase and in the phase-coexistence region directly adjacent (within less than 0.02°) to T_n . The kinetics of the relaxation had in this case a strongly pronounced nonexponential character, viz., except for a quasiexponential component with a time $\tau_1 \lesssim 1$ s close to the lifetime of the MBBA photoisomers,¹⁶ the $\Delta\varphi_a(t)$ dependence contained a component with a substantially longer time $\tau_2 = 10\text{--}30$ min which depended apparently on the intensity of the light.

After entering the two-phase region and passing through the critical-behavior region, $\Delta\varphi_a$ decreased linearly with increase of T up to the temperature T_i , where $\Delta\varphi_a$ decreased to zero. After passing through the critical region, τ_{eff} decreased to its values in the mesophase and the τ_2 component vanished. An insignificant increase of τ_{eff} was observed with further rise of temperature.

3. DISCUSSION

To describe the results rigorously it is necessary to determine the cubic optical nonlinearity in the two-phase region, always a difficult task. We confine ourselves therefore to model-based considerations.

The main processes due to absorption of light in the medium and leading to a change of φ_a are its heating and excitation of MBBA photoisomers. Let us examine the mechanisms of both.

The optically induced NP temperature change, the stationary value of which can be estimated at¹⁷

$$\Delta T \approx \beta \rho_{\text{ex}}^2 I_{\text{ex}} / 4\pi^2 \chi \quad (6)$$

(χ is the NP thermal conductivity) causes the operating point (c'_0, T_0) on the $c' - T$ phase diagram to shift by an amount $\Delta T(I_{\text{ex}})$ along the T axis (Fig. 1). This decreases the NP thickness by increasing the thickness of the isotropic-liquid layers. In addition, the impurity density changes in both phases, and the refractive index of both phases because their polarizability differs from that of the matrix.

In accord with (5), the change Δz_n^{th} is given by

$$\Delta z_n^{\text{th}} = \frac{\partial z_n}{\partial T} \Delta T(I_{\text{ex}}) \equiv \frac{L c'_0}{c'_{i0} - c'_{n0}} \frac{\Delta T(I_{\text{ex}})}{T_c - T}, \quad (7)$$

where ΔT is given by (6).

The stationary value of ΔT in the two-phase region is practically independent of temperature. The change of the difference $T_c - T$ in the interval where the two-phase region exist is also insignificant, so that at the given intensity Δz_n can be regarded as constant.

The anisotropy change of laser-heated NP is determined by the change of $c'_{n,i}$ by an amount $\Delta c'_{n,i} = \Delta T, T_{\text{co}} \alpha_{n,i}$. It follows from (4) that this change is

$$\Delta n_a^{\text{th}} = \frac{4\pi(N_n + N_n') F h \Delta T(I_{\text{ex}})}{2n^e n^o T_{\text{co}} \alpha_n V_n} \left[(\gamma' - \gamma) n_a + \frac{1}{3} (n^e + 2n^o) s(\gamma' - \gamma) \right]. \quad (8)$$

The above expression was obtained by neglecting the weak $s(c'_n)$ dependence. The parameters in (8) depend little on temperature, and Δn_a^{th} can be regarded as constant.

We consider now qualitatively the processes induced in the two-phase region by photoionization of the molecules. If the photoisomers, which can be regarded as optically induced (OI) impurities,² were to interact with the matrix molecules in the same way as the real impurities, their onset would alter the volumes of the corresponding phases without change of the values of c'_n and c'_i . Since, however, the OI interact with the matrix in a manner different from that of the real impurities, the equilibrium densities of the latter change. It is reasonable to assume that since the NP order parameter in the two-phase region is independent of the impurity density (see Sec. 1), excitation of the OI produces an additional phase redistribution such that the order parameter of the system remains unchanged. This assumption means that the appearance of OI can be phenomenologically described by a certain equivalent change of the joint impurity density, i.e.,

$$\tilde{c}' = c'_0 + p c_p, \quad s(\tilde{c}') = s(c'(T_0)). \quad (9)$$

Photoisomer excitation leads consequently to a shift of the operating point (c'_0, T_0) on the phase diagram by an amount $\Delta c'_p$ proportional in first-order approximation to c_p (Fig. 1). This shift, just as in the case of laser heating, leads to a redistribution of the NP and IP thicknesses

$$\Delta z_n^c = -\Delta z_i^c = \frac{\partial z_n^c}{\partial c'} \Delta c' = p c_p(I_{\text{ex}}) T_{\text{co}} \left/ \left(\frac{1}{\alpha_i} - \frac{1}{\alpha_n} \right) \right., \quad (10)$$

where

$$c_p \approx \beta \tau_i \eta I_{\text{ex}} / c_n' \hbar \omega. \quad (11)$$

η is the photoisomerization efficiency and τ_i is the photoisomer lifetime. Just as Δz_n^{th} , the change Δz_n^c depends little on the temperature.

According to the lever rule, a shift of the operating point along the c' axis does not lead in a one-component impurity system to a change of the equilibrium values of c'_n and c'_i [see (2)]. However, redistribution of impurity molecules among the phases, meaning also a change of their refractive indices, will nevertheless take place, since some of the real impurity molecules is replaced by OI, and the polarizabilities of the two types of impurity are different.

Recognizing the additivity of the refraction and using the condition (9), we obtain

$$\Delta n_a^c = \frac{4\pi N_n F \hbar c_p(I_{ex})}{2n^e n^o} \left[(\Delta\gamma_p + p\Delta\gamma) n_o + \frac{1}{3} (n^c + 2n^o) (\Delta\gamma_{pa} + p\Delta\gamma_a) s \right], \quad (12)$$

where $\Delta\gamma_p = \gamma_p - \gamma$ and $\Delta\gamma_{pa} = \gamma_{pa} - \gamma_a$, while γ_p and γ_{pa} are the polarizability and the polarizability anisotropy of the impurity molecule. Just as Δz_n^c , Δn_a^{th} , and Δn_a^c , the value of Δn_a^c in the two-phase region is practically independent of temperature.

Both optically induced heating and photoisomerization lead thus to approximately the same results—redistribution of the volumes of NP and IP and change of their refractive indices. Each of these processes initiates a change in the phase shift of the radiation passing through the medium:

$$\Delta\varphi_a(I_{ex}) = (2\pi/\lambda) (n_a \Delta z_n + z_n \Delta n_a + \Delta n_a \Delta z_n), \quad (13)$$

where

$$\Delta n_a = \Delta n_a^{\text{th}} + \Delta n_a^c \text{ and } \Delta z_n = \Delta z_n^{\text{th}} + \Delta z_n^c.$$

The term Δz_n^c in this expression corresponds to a mechanism analogous to the usual conformational nonlinearity of the mesophase. In fact, the decrease of the NP thickness can be regarded as the maximum possible change of the order parameter from $s(T) \approx s_0(T_c)$ to zero, i.e., it can correspond to a jump of the NP anisotropy from $n_a(T)$ to zero in the region where the IP appears. The second term, connected with photoisomer excitation, has no analog in either the mesophase or the isotropic state of pure NLC, and is determined by the redistribution of the true impurities and the SP among the NP and IP.

The mechanism of the thermal nonlinearity (the terms proportional to Δz_n^{th} and Δn_a^{th}) is also different from the corresponding mechanism in the mesophase and in an isotropic liquid, where it is determined by the small derivative dn/dT . In fact, laser heating in the two-phase region, just as in the case of conformational nonlinearity, leads to redistribution of the impurities and can therefore have comparable inefficiency with the conformation mechanism. The contributions of the thermal and conformational nonlinearities to $\Delta\varphi_a$ depend on the specific experimental setup, on the NLC and SP parameters, and on the actual impurities.

Expressions (7)–(13) describe the experimental results qualitatively. In fact, as shown above, the values of Δz_n and Δn_a depend little on the temperature, and the NP thickness z_n decreases linearly from the value $z_n = L$ at $T = T_n$ to zero at the point $T = T_i$. The change of the birefringence is therefore not determined by the temperature-dependent term $n_a \Delta z_n$ and by the linearly decreasing term $z_n \Delta n_a$, i.e., $\Delta\varphi_a$ should decrease linearly with increase of T and vanish jumpwise when the temperature T_i is reached. This is precisely the dependence obtained in experiment (See Fig. 5).

The proposed model explains also the obtained $\Delta\varphi_a(I_{ex})$ dependence. At low values if I_{ex} the quadratic term in (13) can be neglected and $\Delta\varphi_a \sim I_{ex}$. At high exciting-light intensities the term $\Delta n_a \Delta z_n \sim I_{ex}^2$ becomes substantial, leading to a deviation of the experimental dependence from linearity. With further increase of I_{ex} the optically induced change Δz_n reaches the value z_n , and this leads to vanishing of the NP and of the signal I_i^{out} .

We consider now the establishment of the stationary

value of φ_a^s . In the case of the purely thermal nonlinearity mechanism, turning on the light abruptly first establishes a stationary temperature distribution (it is determined by the time of heat diffusion over the cell thickness, depends on the NP heat capacity, is of the order of 1 ms, and increases radically near T_n , Ref. 18). When the stationary value of the temperature is established, redistribution of the impurities and of the actual molecules of the crystal sets in and leads to changes of z_n and z_i . These times are determined by the impurity-diffusion and self-diffusion coefficients of the MBBA molecules and should be of the order of the time of diffusion of this molecule over the cell thickness. Far from the critical points, the diffusion coefficients are $D = 10^{-6}$ – 10^{-7} cm²/s (Refs. 19, 20) and the corresponding characteristic times are $\tau_{\text{eff}} = L/2\pi D = 0.1$ – 1.0 s. Near the point $T = T_n$, which is in fact the phase-stratification point, the molecule diffusion slows down radically,²¹ leading in fact to the observed abrupt increase of the time of establishment of z_n and n_a near T_n .

If furthermore a nonlinearity conformation mechanism is also present, an additional characteristic time of stationary SP density establishment appears and is determined by the SP lifetime and diffusion coefficient.

The reasoning above agrees qualitatively with experiment. Since the time resolution of the plotter for the kinetics is $\Delta\varphi_a(t) \approx 10^{-2}$ s, we recorded only the characteristic times corresponding to redistribution of the actual impurity and isomer molecules. The abrupt growth of τ_{eff} near T_n is due to the slowing down of the diffusion near the phase-stratification point, while the nonexponential character of the kinetics inside the two-phase region is connected with several mechanism that establish $\Delta\varphi_a$. It is possible that τ_{eff} increases insignificantly as T_i is approached because a single time was incorrectly introduced for the nonexponential $\Delta\varphi_a(t)$ dependence and because the relation between the various mechanisms of φ_a variation vary with temperature.

We present a few estimates. To find Δz_n we use the fact that $\Delta\varphi_a$ near T_i is determined by the term $n_a \Delta z_n$ [see (13)]. At $I_{ex} \approx 0.1$ W/cm² we have $\Delta\varphi_a \approx 0.6$, which correspond to a thickness change $\Delta z_n \approx 0.3$ μm ($\lambda_i = 0.63$ μm , $n_a \approx 0.2$). From the same dependence we can estimate also Δn_a by measuring in addition the value of $\Delta\varphi_a$ near $T = T_n$:

$$\frac{\Delta\varphi_a(T=T_n)}{\Delta\varphi_a(T=T_i)} \approx \frac{L\Delta n_a + n_a \Delta z_n}{n_a \Delta z_n}.$$

It should be noted that it is incorrect to estimate Δn_a directly using $\Delta\varphi_a(T = T_n)$, since τ_{eff} increases drastically near T_n (see Fig. 6). As a rough estimate we used therefore the value obtained for $\Delta\varphi_a$ by extrapolating $\Delta\varphi_a(T)$ far from the singular points to the temperature T_n . In this case $\Delta\varphi_a(T = T_n)/\Delta\varphi_a(T = T_i) \approx 5$ and $\Delta n_a \approx 10^{-3}$.

The estimates obtained for Δz_n and Δn_a agree with the $\Delta\varphi_a(I_{ex})$ dependence. In fact, at $I_{ex} \approx 0.8$ W/cm², when the increase of $\Delta\varphi_a$ becomes faster than linear, the nonlinear term is about 20% of the linear, i.e., the two are comparable. The intensity $I_{ex} = 1$ to 2 W/cm² at which the change of $\Delta\varphi_a$ drops suddenly to zero corresponds to the NP thickness $\Delta z_n \approx 3$ – 6 μm at the measurement temperature ($z_n \approx 10$ μm).

As indicated above, the contributions to the total thermal and conformational mechanisms can be comparable. We present the corresponding estimates.

The relation between the thermal and conformation contributions to $\Delta\varphi_a$ is described, in accordance with (7) and (10), by the relation

$$\frac{\Delta z_n^{\text{th}}}{\Delta z_n^c} = \frac{\Delta T(I_{\text{ex}})}{T - T_c} \frac{c'}{p c_p(I_{\text{ex}})} = \frac{\rho_{\text{ex}}^2 N_n c' \hbar \omega}{\pi^2 V_n \chi \eta \tau_i p (T - T_c)}. \quad (14)$$

All the parameters but in this expression are known ($\chi = 2.1 \cdot 10^{-14} \text{ erg} \cdot \text{s}^{-1} \cdot \text{cm}^{-1} \cdot \text{deg}^{-1}$ (Ref. 18), $\eta = 3$ (Ref. 16), $\tau_i = 1 \text{ s}$ (Ref. 15), and $N_n/V_n = 2.4 \cdot 10^{21} \text{ cm}^{-3}$). To estimate the coefficient p we use the fact that it should equal the ratio⁸

$$\frac{\Delta \tilde{\nu}_p}{\Delta \tilde{\nu}} = \frac{\tilde{\nu}_{11} - \tilde{\nu}_{12p}}{\tilde{\nu}_{11} - \tilde{\nu}_{12}},$$

where $\tilde{\nu}_{12p}$ is the orientational part of the interaction between the photorotated and proper molecules of MBBA. We have shown earlier² that the shift of the temperature T_c of a pure NLC following addition of impurity molecules is given by

$$\Delta T_c \approx c' \frac{\Delta \tilde{\nu}}{\tilde{\nu}_{11}} T_c.$$

It follows hence that

$$\frac{\Delta \tilde{\nu}}{\Delta \tilde{\nu}_p} \approx \frac{\Delta T_c(c') c_p}{\Delta T_c(c_p) c'}.$$

In our case $\Delta T_c(c')/c' \approx 200 \text{ deg}$ and $\Delta T_c(c_p)/c_p \approx 3 \text{ deg}$ (Ref. 2), therefore $p \approx 1.5 \cdot 10^{-2}$. Substituting this parameter and others in (14) we get $\Delta z_n^{\text{th}}/\Delta z_n^c \approx 10$, i.e., in contrast to the mesophase the contribution of the thermal mechanism to the nonlinearity is substantial, a fact determined for the most part by the smallness of the parameter p .

Similar estimates of the change of the refractive index also show that the values of Δn^{th} and Δn^c are comparable.

CONCLUSIONS

Thus, construction of sandwich structures that are homogeneous in the two-phase region has made it possible to investigate the optical sensitivity of the region of existence of NP and IP of an impurity NLC to light. Among the principal results of these investigations are the following.

1. It was observed that absorption of light in the two-phase region leads to optically induced variations of the refractive index and of the volumes of the coexisting phases, due to heating of the medium and excitation of SP.

2. In the presence of thermal nonlinearity the changes of the volumes of the NP and IP are due to the changes of the equilibrium densities c'_i and c'_n in these phases as a result of heating the medium. Changes of c'_i and c'_n are produced also by changes of the refractive indices n_i and n_n due to inequality of the polarizabilities of the matrix and of the impurity.

3. In the presence of conformational nonlinearity, excitation of the SP also leads to a redistribution of the phase values on account of the increase of the total number of im-

purity molecules in the system. The values of n_i and n_n are also changed, since the polarizability of the SP differs from that of the intrinsic impurities and the matrix molecules, and also because part of the intrinsic-impurity molecules is replaced by photoisomers.

We note in conclusion that the use of samples with sandwich structure and of nonlinear-optics methods leads to a new original and quite sensitive method of investigating the two-phase region. In particular, by varying the parameters of the applied radiation it is possible to vary in a wide impurity-density range the rate of their creation and their spatial distribution. This permits an investigation of the kinetics of the onset of thermodynamic equilibrium in the two-phase region, of transport processes, of thermal diffusion, and others.

The authors thank O. D. Lavrentovich, A. I. Khizhnyak, and the participants of the Moscow seminar on liquid-crystal physics for useful discussions.

- ¹ B. Ya. Zel'dovich and N. V. Tabiryan, *Usp. Fiz. Nauk* **147**, 633 (1985) [*Sov. Phys. Usp.* **28**, 1059 (1985)].
- ² I. P. Pinkevich, Yu. A. Reznikov, V. Yu. Reshetnyak, and O. V. Yaroshchuk, *Conformational Optical Nonlinearity of Crystals*, Preprint No. N18, Ukrainian Academy of Sciences, Kiev, 1990.
- ³ S. G. Odulov, Yu. A. Reznikov, M. S. Soskin, and A. I. Khizhnyak, *Zh. Eksp. Teor. Fiz.* **85**, No. 6 (1988) [*Sov. Phys. JETP* **58**, No. 6 (1988)].
- ⁴ M. P. Pinkevich, Yu. A. Reznikov, V. Yu. Reshetnyak, A. I. Khizhnyak, and O. V. Yaroshchuk, *ibid.* **96**, No. 3 (1989) [**59**, No. 3 (1989)].
- ⁵ P. Palffy-Muhoray, D. A. Dunmur, and A. Price, *Chem. Phys. Lett.* **93**, No. 6, 572 (1982).
- ⁶ D. E. Martire, G. A. Oweimreen, G. I. Agren, S. S. Ryon, and U. T. Peterson, *J. Chem. Phys.* **66**, No. 4, 1456 (1976).
- ⁷ M. A. Anisimov, R. R. Bashirov, and Z. R. Gadzhieva, *Kristallografiya* **33**, 492 (1989) [*Sov. Phys. Crystallogr.* **33**, 290 (1988)].
- ⁸ Yu. A. Reznikov, V. Yu. Reshetnyak, O. V. Yaroshchuk, and V. V. Lutkovskii, *Conformational Nonlinearity in Two-Phase Region of MBBA*, Preprint No. N21, Phys. Inst. Ukr. Acad. of Sciences, Kiev, 1989.
- ⁹ A. E. Kohler, *Z. Phys. Chemie* **268**, No. 6, 1091 (1987).
- ¹⁰ A. E. Kohler, *ibid.* **260**, No. 2, 347 (1979).
- ¹¹ W. H. de Jeu, *Physical Properties of Liquid-Crystal Materials*, Gordon & Breach, 1980.
- ¹² G. R. Luckhurst, *Liq. Cryst.* **2**, No. 4, 441 (1987).
- ¹³ V. N. Matveenko and E. A. Kirsanov, *Surface Phenomena in Liquid Crystals*, Moscow Univ., 1991.
- ¹⁴ A. I. Khizhnyak, I. P. Pinkevich, Yu. A. Reznikov, V. Yu. Reshetnyak, and O. V. Yaroshchuk, *Soc. Phot. Instrum. Eng.* **1183**, 210 (1990).
- ¹⁵ G. O. Puchkos'ka, Yu. O. Reznikov, and O. V. Yaroshchuk, *Usp. Fiz. Nauk* **34**, No. 7, 1036 (1989) [*sic*].
- ¹⁶ I. P. Pinkevich, Yu. A. Reznikov, V. Yu. Reshetnyak, A. I. Khizhnyak, and O. V. Yaroshchuk, *Opt. Spekt.* **67**, No. 4, 753 (1989).
- ¹⁷ L. Richard, J. Maurin, and J. P. Nuighard, *Opt. Comm.* **57**, No. 5, 365 (1986).
- ¹⁸ P. Dorion, J. R. Labanne, and B. Pouligny, *Mol. Cryst. Liq. Cryst.* **144**, 169 (1987).
- ¹⁹ M. A. Reznikov, V. Yu. Reshetnyak, and O. V. Yaroshchuk, *Dokl. AN UkrSSR*, ser. A, No. 8, 51 (1988).
- ²⁰ H. Hervet, W. Urbach, and F. Rondelez, *J. Chem. Phys.* **86**, No. 6, 2725 (1978).
- ²¹ M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* [in Russian], Nauka, 1987.

Translated by J. G. Adashko