Photoinduced conversions in nematic liquid crystals with a long excited-state lifetime

O. A. Shustin, T. G. Chernevich, A. I. Fedorova, and I. A. Yakovlev
M. V. Lomonosov State University, Moscow

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A new type of reversible, long-lived photoinduced conversion of crystals has been discovered in two nematic liquid crystals which belong to the class of azoxy compounds (BMAOB and BGAOB).

1. Two mechanisms are known for photoinduced changes in the refractive index in nematic liquid crystals. First, there is the orientational nonlinearity mechanism which involves a rotation of the director of a liquid crystal caused by the field of a light wave.[1,2] Second, there is the nonlinearity, discovered in MBBA, which is caused by photoconversions of the crystal molecules which result in changes in the polarizability of the molecules and in the order parameter of the crystal.[3]

We have now discovered a new type of reversible photoinduced conversion of a crystal, in two nematic liquid crystals belonging to the class of azoxy compounds (BMAOB and BGAOB) and also in their mixture, the crystal ZhK-440. In this case the lifetime of the converted state reaches several minutes, more than two orders of magnitude longer than the lifetime of the photoconverted form of the molecules of the MBBA crystal, discovered in Ref. 3.

The data reported below refer to the temperature region near the nematic→(isotropic liquid) phase transition, where the effect is at a maximum. We restrict the present discussion to the results for the BMAOB crystal.

Two methods were used to study photoconversions in the crystal: 1) measurement of the intensity of the diffraction and self-diffraction of light by a photoinduced grating in the crystal; 2) measurement of the time dependence of the birefringence of the crystal when the light beam illuminating the crystal is turned on and off.

2. To create the photoinduced grating, we used two unfocused coherent light beams from an argon laser ($\lambda = 5145$ Å, with an intensity ratio of 1:1.5), which meet at a small angle in the liquid-crystal sample and which are incident nearly along the normal to the plane of the cell. The lattice constant d is varied from 0.04 to 0.19 mm. The average power density of the light incident on the crystal is varied from 0.2 to 6.0 W/cm^2. We study both the self-diffraction of the beams from the argon laser and the diffraction of a weak probing beam from a helium-neon laser ($\lambda = 6328$ Å). We use planar-oriented crystal samples, held in a cell 100 μm thick. The temperature of the sample, held in an oven, is regulated within 0.02 °C. The measurements are taken in the following versions of the experimental geometry: 1) $\mathbf{n}\|\mathbf{i},\mathbf{n}\perp\mathbf{d}$; 2)$\mathbf{n}\perp\mathbf{i},\mathbf{n}\perp\mathbf{d}$; 3) $\mathbf{n}\|\mathbf{i},\mathbf{n}\|\mathbf{d}$; 4)$\mathbf{n}\perp\mathbf{i},\mathbf{n}\|\mathbf{d}$, where $\mathbf{n}$ is the director, $\mathbf{i}$ is the polarization vector of the light beams which create the grating, and $\mathbf{d}$ is the lattice vector.

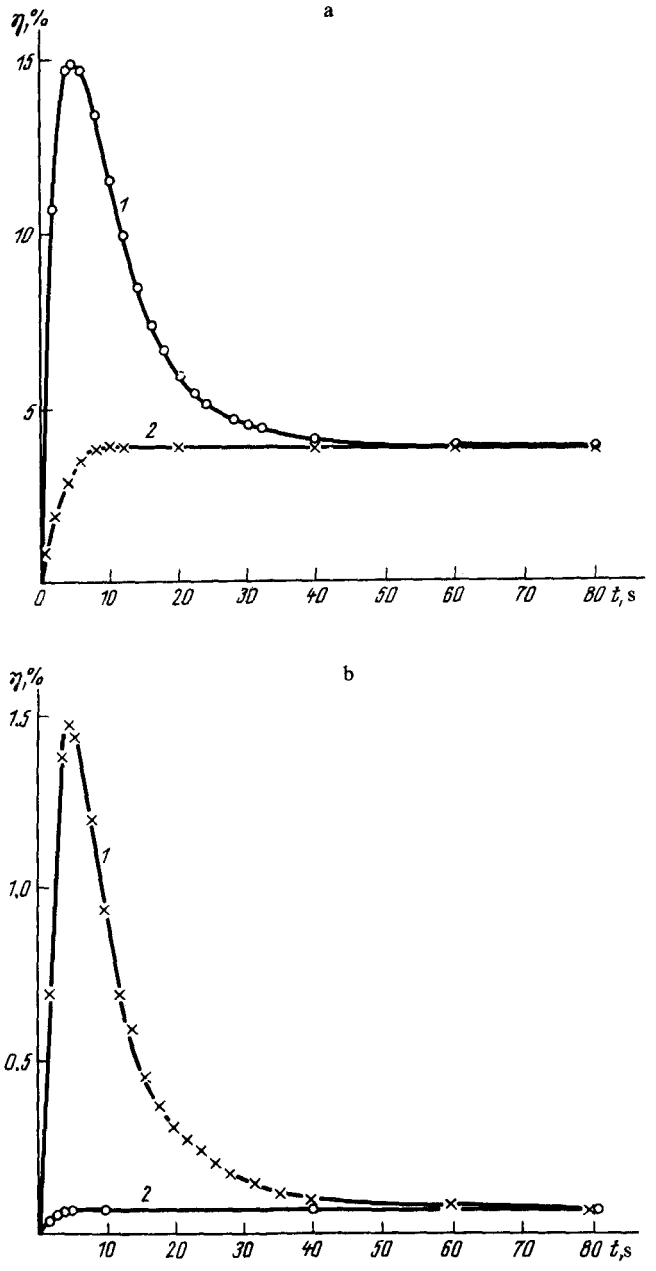

FIG. 1. Diffraction efficiency versus the recording time. a—Geometric version 1); b—geometric version 2).

3. The results show that the process of the recording of the photoinduced grating depends on whether the crystal is illuminated beforehand. If it is not illuminated for a time interval Δt, after which the two beams are turned on simultaneously, the time evolution of the diffraction efficiency (η) of the grating is nonmonotonic, going

through a maximum intensity η_{max} and then becoming constant at η_0 (curve 1 in Fig. 1). If the crystal is illuminated beforehand by one of the light beams, and then the other is turned on, the time evolution of the diffraction efficiency is monotonic (curve 2 in Fig. 1) and can be described quite well by the expression $[1-\exp(-t/\tau)]^2$ with a recording scale time $\tau = 2$ s. The value of η reaches the same value as in the first version of the recording, η_0. Figures 1a and 1b show experimental data for versions 1) and 2) of the experimental geometry (the lattice constant is $d = 0.087$ mm; and average power density is 3.5 W/cm^2; $\Delta t = 10$ min; and the crystal temperature is $\Delta T = T_c - T = 0.7$ °C). It follows from Fig. 1 that the value of η_0 for geometric version 1) is about two orders of magnitude higher than η_0 in version 2), at the same crystal temperature. The ratio η_{max}/η_0, however, is significantly larger in the second case. As the time interval Δt is increased, the ratio η_{max}/η_0 increases, while η_0 remains constant at a fixed experimental temperature (Fig. 2). The intensity of the self-diffraction when one of the light beams is turned off or the intensity of the diffraction of the probing beam when the two beams creating the grating are turned off simultaneously falls off in accordance with the exponential law $\exp(-2t/\tau)$ with a scale time $\tau = 2$ s.

4. A mathematical analysis of the experimental results based on a solution of the system of kinetic equations, which will be described in detail elsewhere, leads to the conclusion that the appearance of the photoinduced grating in these crystals is due primarily to long-lived photoconversions of molecules of the crystals. Furthermore, the lifetime (θ) of the photoinduced state is significantly longer than the scale times for the photoconversion ($\tau_I \equiv 1/\alpha I$, where the factor α is proportional to the absorption coefficient, and I is the power density of the light incident on the crystal) and the diffusion of the excited molecules ($\tau_g \equiv 1/q^2 D$, where D is the diffusion coefficient, and $q = 2\pi/d$).

These conclusions are supported by experiments on the dependence of the observed effect on the lattice.

The reason for the decrease in η with increasing recording time after passage through the maximum is that diffusion partially erases the difference in the concentra-

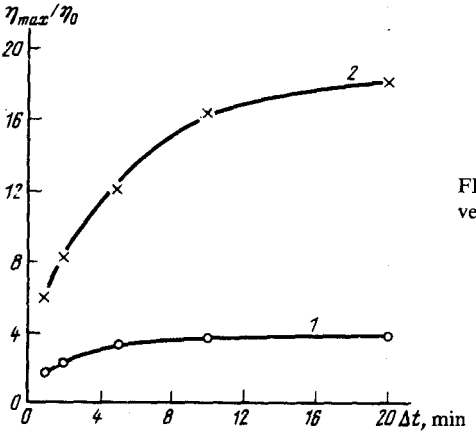

FIG. 2. η_{max}/η_0 versus Δt. 1—Geometric version 1); 2—version 2).

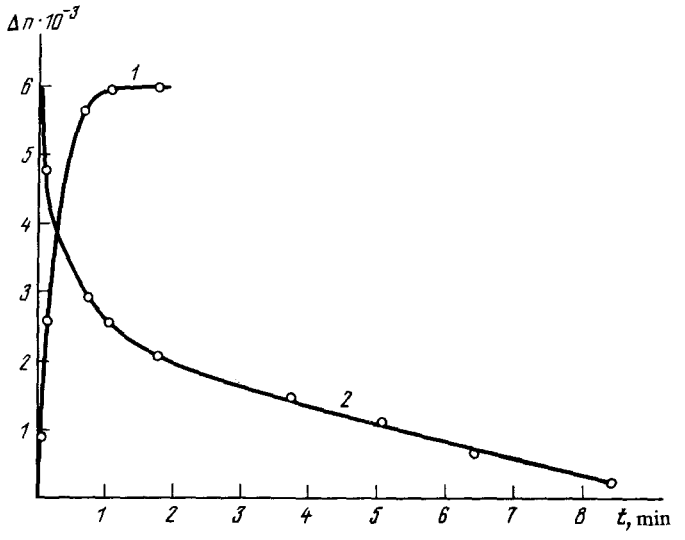

FIG. 3. Birefringence of the crystal versus the illumination time ($\mathbf{i} \| \mathbf{n}$). 1—Light is turned on; 2—off.

tions of photoconverted molecules in the illuminated and unilluminated parts of the crystal.

We estimate the lifetime θ to be ~ 5 min. The corresponding values of τ_I and τ_g are ~ 8 and ~ 3 s for the experimental conditions listed above. We also calculated the diffusion coefficient parallel to and perpendicular to the director: $D_{\|} = (10 \pm 1) \times 10^{-7}$ cm^2/s and $D_{\perp} = (7 \pm 1) \times 10^{-7}$ cm^2/s.

5. The appearance of a long-lived photoinduced state of the crystal has been confirmed by an independent experiment in which a liquid-crystal cell was placed between crossed polarizers. The polarization plane of the weak probing beam from the helium-neon laser, incident normally on the cell, made an angle of 45° with the principal directions of the polarizer and the analyzer. We measured the time evolution of the intensity of this beam as the light beam from the argon laser, with a power density of 1.3 W/cm^2, was turned on and off. From the results we can calculate the time evolution of the birefringence (Δn) of the crystal (Fig. 3). The scale time for the photoconversion and the lifetime of the photoconverted state are $\tau_I = 20$ s and $\theta = 5$ min, in good agreement with estimates of these times from our experiments with the photoinduced gratings. In this case the increase in τ_I is due to the lower power density.

The mechanism described above for a photoinduced change in the refractive index is the governing mechanism for these particular crystals, but it is apparently not the only mechanism. There are some other possible processes which could make some contribution to the observed effect (e.g., a thermal effect of the light).

[1]B. Ya. Zel'dovich, N. F. Pilipetskiĭ, A. V. Sukhov, and N. V. Tabiryan, Pis'ma Zh. Eksp. Teor. Fiz. **31**, 287 (1980) [JETP Lett. **31**, 263 (1980)].

[2]A. S. Zolot'ko, V. F. Kitaeva, N. Kroo, N. N. Sobolev, and L. Chilaya, Pis'ma Zh. Eksp. Teor. Fiz. **32**, 170 (1980) [JETP Lett. **32**, 158 (1980)].
[3]S. G. Odulov, Yu. A. Reznikov, M. S. Soskin, and A. I. Khizhnyak, Zh. Eksp. Teor. Fiz. **82**, 1475 (1982) [Sov. Phys. JETP **55**, 854 (1982)].

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