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Tricritical-like behavior of the nonlinear optical refraction at the nematic-isotropic transition in the E7 thermotropic liquid crystal

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Abstract. We use Z-scan technique to investigate the nonlinear optical response of the thermotropic liquid crystal E7 in the neighborhood of the nematic-isotropic phase transition. The analysis of the data for the nonlinear optical birefringence is compatible with an effective critical exponent of the order parameter, $\beta = 0.28 \pm 0.03$, which is close to the classical value, $\beta = 0.25$, for a tricritical point. The nonlinear optical absorption in the nematic range depends on the geometrical configuration of the nematic director with respect to the polarization beam, and vanishes in the isotropic phase.

1 Introduction

Nematic-Isotropic (N-I) phase transitions, which are among the most investigated phenomena in liquid crystals, still pose some interesting problems. According to the Landau-de Gennes theory, symmetry requirements of the nematic quadrupolar interactions lead to a first-order phase transition, with a jump of the nematic order parameter at the transition temperature [1,2]. This jump, however, is in general quite small. Measurements of enthalpy and volume changes at the transition, as compared with experimental results at melting, fully support this scenario of a weak first-order phase transition, with strong fluctuations, which may lead to an effective critical behavior and to effective critical exponents [3–7]. Although there are no systematic and conclusive studies on this thermodynamic behavior, some experimental analyses indicate the occurrence of tricritical rather than just critical effective exponents [8].

The N-I transition has been experimentally studied by various techniques, including light scattering, Kerr effect, polarized light microscopy, and calorimetry. Although there are some disagreements, most of these investigations support the tricritical hypothesis [8]. Techniques of nonlinear optics, however, have not received much attention in this context. Among the numerous techniques for studying the nonlinear optical properties of a medium, the Z-scan technique [9], which is recognized by its simplicity, leads to the determination of the nonlinear optical parameters for different time scales.

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The main purpose of this article is to report the use of the Z-scan technique to investigate the nonlinear refraction index of the well-known thermotropic liquid crystal E7 in the neighborhood of the N-I phase transition. In sect. 2, we describe experimental details and the Z-scan technique. In sect. 3, we discuss the experimental results and some conclusions are presented in the last section.

2 Experimental details

The liquid-crystalline system E7 (Merck) is a well-known commercial mixture of biphenyls and triphenyls, composed mainly by 5CB ($\sim$ 51%), which was used without further purification [10]. It displays a nematic phase between $-10\,^{\circ}$C and the transition temperature to the isotropic phase, at $T_{\mathrm{NI}} = 58\,^{\circ}$C. The samples of the liquid crystal were conditioned in a parallel glass cell, separated by $20\,\mu$m thick spacers. The glass plates were coated with PVA (polyvinyl alcohol) and buffed for homogeneous planar alignment of the liquid crystal. The sample was placed in a hot stage (INSTEC) on a computer-controlled translational stage (Newport). The temperature of the sample was controlled with a precision of 0.2°C.

2.1 Z-scan technique

A TEM_{00} laser beam incident in a nonlinear refractive medium self-induces a radially symmetric phase variation $\Delta\phi\,(r)$ of the beam leading to a diffraction pattern. In the case of a cubic nonlinearity, the refraction index can

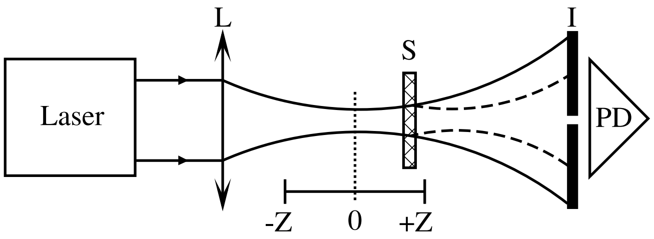

Fig. 1. Sketch of the Z-scan apparatus in the closed-aperture configuration. L is the lens, S is the sample, I is the iris, and PD is the photodetector.

be written as $n = n_0 + n_2 I$ where n_0 and n_2 are the linear and the nonlinear refraction index, respectively [11]. A medium can also exhibit a nonlinear optical absorption. In the case of a two-photon absorption process, the absorption coefficient is written as $\alpha = \alpha_0 + \alpha_2 I$, where α_0 and α_2 are the linear and nonlinear absorption coefficients, respectively. The Z-scan technique [9] exploits the formation of a lens with variable focal length in a nonlinear refractive medium when illuminated by a tight Gaussian-profile laser beam. The magnitude and sign of the nonlinear refraction n_2, and nonlinear absorption α_2 can be obtained by means of two independent measurements, the closed-aperture Z-scan configuration, and the open-aperture Z-scan configuration, respectively, which are two different experimental setups of the Z-scan technique. Figure 1 shows a sketch of the setup in the closed-aperture configuration. In this setup the transmitted intensity is measured behind an iris centered along the z-axis. A medium characterized by $n_2 > 0$ (< 0) behavies like a positive (negative) lens. On the other hand, in the open-aperture setup the totality of the transmitted light at the exit of the sample is collected and measured, rendered insensitive to nonlinear refraction. In systems that exhibit both nonlinear refraction and nonlinear absorption, with the assumptions of local cubic nonlinearity, sufficiently thin sample, to first-order corrections in the irradiance of a Gaussian laser beam, and at the far field condition, the normalized transmittance in the closed-aperture ($\mathit{\Gamma}_c$) and open-aperture ($\mathit{\Gamma}_o$) configurations of the Z-scan technique are given, respectively, by [9,12]

$$\mathit{\Gamma}_c = 1 - \frac{4\mathit{\Phi}\left(\frac{z}{z_o}\right)}{\left[1+\left(\frac{z}{z_o}\right)^2\right]\left[9+\left(\frac{z}{z_o}\right)^2\right]} - \frac{\mathit{\Theta}\left[\left(3+\left(\frac{z}{z_o}\right)^2\right)\right]}{\left[1+\left(\frac{z}{z_o}\right)^2\right]\left[9+\left(\frac{z}{z_o}\right)^2\right]} \tag{1}$$

and

$$\mathit{\Gamma}_o = 1 - \frac{1}{2}\frac{\mathit{\Theta}}{\left[1+\left(\frac{z}{z_o}\right)^2\right]}, \tag{2}$$

where z_o is the Rayleigh range of the beam, $\mathit{\Phi} = k n_2 I_o L_{ef}$, $\mathit{\Theta} = \alpha_2 I_o L_{ef}$, k is the wave number, $L_{ef} = [1-\exp(-\alpha_o L)]/\alpha_o$ is the effective thickness of the sample, and I_o is the irradiance at the beam waist of the laser. Thus, for obtaining the coefficient n_2 at each temperature, we perform two types of independent measurements, open-aperture and closed-aperture Z-scan, at the same power of the laser beam. However under incidence of a moderated-power cw laser beam, the nonlinearity in a nematic liquid crystals is essentially from thermal origin due to the temperature dependence of the order parameter S. It is said that the laser induce a Thermal Lens and the intensity of this effect is proportional to the thermooptical coefficient $\mathrm{d}n/\mathrm{d}T$ [13], *i.e.* the refraction index can be written as $n = n_0 + (\mathrm{d}n/\mathrm{d}T)\,\mathit{\Delta} T$, where $\mathit{\Delta} T$ is the change in temperature [14]. Although the diffusion of heat leads to a phase variation of the laser beam which does not match exactly its intensity spatial profile, for samples with low absorption and low thermal conductivity, it was shown [15] that the Sheik-Bahae's model for the Z-scan experiment, based in a purely local effect, gives a good description of the transmittance, being possible to write that $\mathrm{d}n/\mathrm{d}T \propto n_2$, where n_2 and $\mathrm{d}n/\mathrm{d}T$ are the fitting parameters of the Sheik-Bahae's model [9] and the thermal lens model, respectively.

Our experimental setup used a cw laser ($\lambda = 532\,\mathrm{nm}$, Verdi, Coherent), and the power changed in the range 3–40 mW. The beam waist at focus was about $26\,\mu\mathrm{m}$, and data acquisition was made *via* an oscilloscope. The polarization ($\mathbf{E}$) of the laser beam was set either parallel or perpendicular to the nematic director ($\mathbf{n}$), so the reorientation of the nematic director by an optical torque ($\boldsymbol{\mathit{\Gamma}}_{\mathrm{opt}} = \mathbf{D} \times \mathbf{E}$) is not expected to occur.

3 results and discussions

In figs. 2(a) and (b), we show typical Z-scan curves for both experimental setups, open-aperture and closed-aperture Z-scan, and for both configurations between nematic director and beam polarization, $\mathbf{n} \parallel \mathbf{E}$ and $\mathbf{n} \perp \mathbf{E}$. Data shown in figs. 2 were obtained at $T = 35\,^\circ\mathrm{C}$. The error bars correspond to the standard error of the mean of ten measurements at least, in each z position. In fig. 3, we show values of n_2 in the nematic and in the isotropic phases, for incident polarization parallel and perpendicular to the director. For $\mathbf{n} \parallel \mathbf{E}$, the sample displays $n_2 < 0$ in the full nematic region, which indicates a self-defocusing effect. On the other hand, for $\mathbf{n} \perp \mathbf{E}$, the sample displays $n_2 > 0$, indicating a self-focusing effect. For both configurations between the nematic director and the polarization of the beam, $|n_2| \sim 10^{-9}\,\mathrm{m^2W^{-1}}$, with increasing values as the N-I transition temperature is approached from below. Although these results are consistent with laser heating of the sample, if the linear absorption were independent of the polarization we should have $n_{2\parallel} = -2n_{2\perp}$, and deviations from this behavior are due to dichroism of the sample. Let us discuss now about the origin of the nonlinear optical response in the E7 liquid crystal in the time scale of our experiment. We checked the nonlinear optical response of the empty glass cell with PVA coating: for the powers used in our experiment ($\sim 30\,\mathrm{mW}$), the cell does

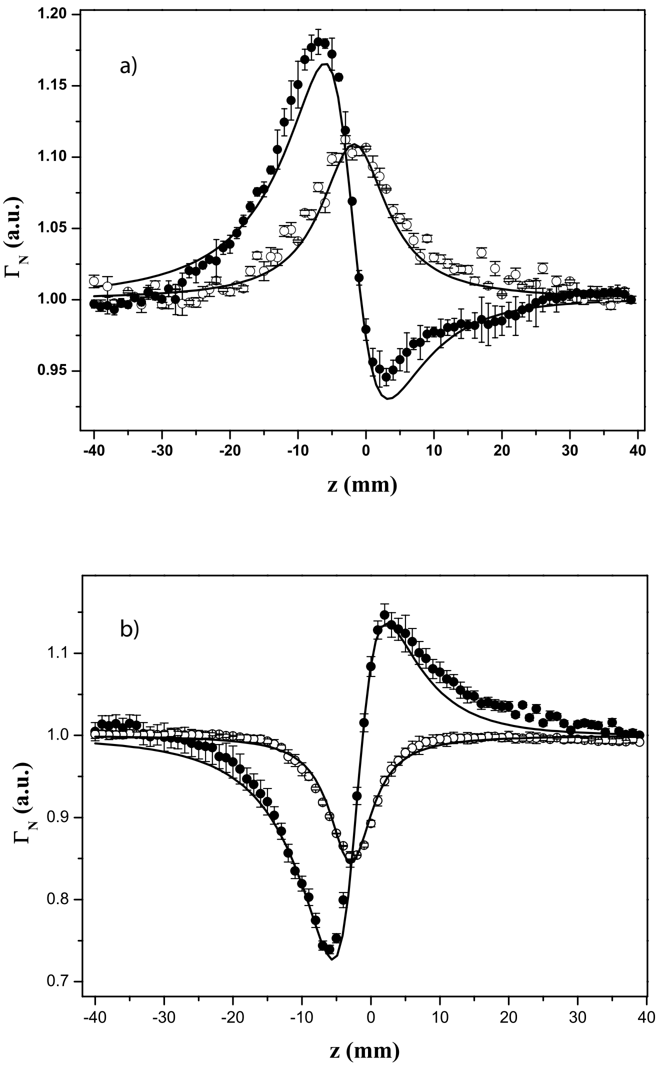

Fig. 2. Typical Z-scan curves in closed-aperture (•) and open-aperture (∘) configurations, at temperature $T = 35\,^{\circ}$C: (a) $\mathbf{n} \parallel \mathbf{E}$; (b) $\mathbf{n} \perp \mathbf{E}$. Note the different peak-valley configurations in both cases, corresponding to n_2, $\alpha_2 < 0$, for $\mathbf{n} \parallel \mathbf{E}$, and n_2, $\alpha_2 > 0$, for $\mathbf{n} \perp \mathbf{E}$. Solid lines are fittings to eqs. (1) and (2).

not show nonlinear optical refraction nor absorption. On the other hand, the dipole moment of 5CB is calculated to be of about $6.5D$ [16] so, the dipolar interaction energy between the optical electric field and the molecules is about 3 orders smaller than the thermal energy, eliminating the possibility of optically induced molecular reorientation. Also, due to the similarity between the dielectric constants and masses of the components of the E7 mixture, we discard any contribution from thermal diffusion (Soret effect) and electrostriction to the nonlinear optical response. Interestingly, for $\lambda = 514\,\mathrm{nm}$, in the nematic phase, and in the ms time scale, 5CB has a negligible nonlinear optical absorption and the nonlinear refraction n_2 is $\sim 10^{-11}\,\mathrm{m^2W^{-1}}$, *i.e.* two orders smaller than in our case [17]. It is known that optical properties like absorption and refractive indices of liquid crystals that consist of

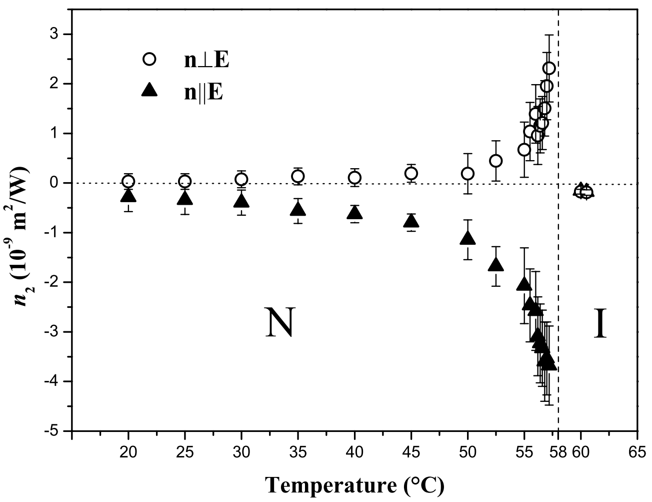

Fig. 3. Nonlinear refraction index n_2 as a function of temperature in the nematic range and in the isotropic phase, for both configurations of the nematic director and the beam polarization, (▲) for $\mathbf{n} \parallel \mathbf{E}$ and (∘) for $\mathbf{n} \perp \mathbf{E}$. The dashed vertical line indicates the transition temperature.

satured and unsatured phenyl rings depend on the characteristics of the spectrum in the UV spectral region, mainly due to the λ_1 and λ_2 bands involving $\pi \rightarrow \pi^*$transitions, having a negligible absorption in the visible region [18]. The constituents of the E7 thermotropic mixture do not exhibit intrinsic band-gap, so there is not absorption by free carriers. So a probable origin of the nonlinear optical response in E7 liquid crystal for a laser of $\lambda = 532\,\mathrm{nm}$ is the excitation of the λ_2 band by the absorption of two photons (TPA) and posterior nonradiative relaxation mechanism. In fig. 4, we show the ratio of the absolute values of n_2 obtained for each geometry as the temperature approaches T_{NI}. We note that $|n_{2\|}/n_{2\perp}|$ tends to 2 near the N-I transition. This is an indication that the entropic contribution to n_2 becomes more important as we get closer to the clearing temperature. Similar behavior was observed in a pure sample of 5CB at the nematic-isotropic transition [19]. At $T = 60\,^{\circ}$C (isotropic phase), $n_2 \sim -0.2 \times 10^{-9}\,\mathrm{m^2W^{-1}}$.

Figure 5 shows the nonlinear birefringence Δn_2 as a function of temperature. As observed for the nonlinear refraction indices, the magnitude of the nonlinear birefringence increases as the NI transition temperature is approached from below (and finally seems to diverge). For typical nematic liquid crystals, de Jeu [20] showed that the linear birefringence $\Delta n = n_{||} - n_{\perp}$ is related to the density ρ and the order parameter S by $\Delta n \backsim \rho^{\frac{1}{2}} S$. Also, it has been observed that the density is almost constant in all the nematic range, so we may write $\frac{\mathrm{d}n_{||}}{\mathrm{d}T} - \frac{\mathrm{d}n_{\perp}}{\mathrm{d}T} \sim \rho^{\frac{1}{2}} \frac{\mathrm{d}S}{\mathrm{d}T}$, from which and from the previous discussion $\Delta n_2 = n_{2||} - n_{2\perp} \propto \frac{\mathrm{d}n_{||}}{\mathrm{d}T} - \frac{\mathrm{d}n_{\perp}}{\mathrm{d}T}$, *i.e.*

$$\Delta n_2 \propto \frac{\mathrm{d}S}{\mathrm{d}T}. \tag{3}$$

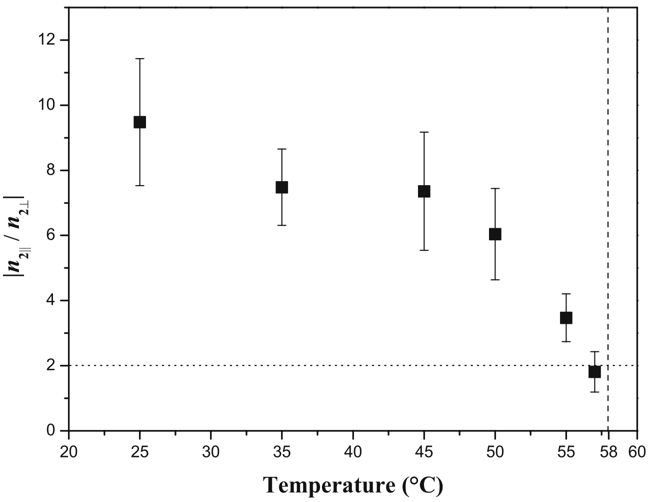

Fig. 4. Ratio of the absolute values of the nonlinear refraction indices in the nematic range. The dashed line indicates the transition temperature.

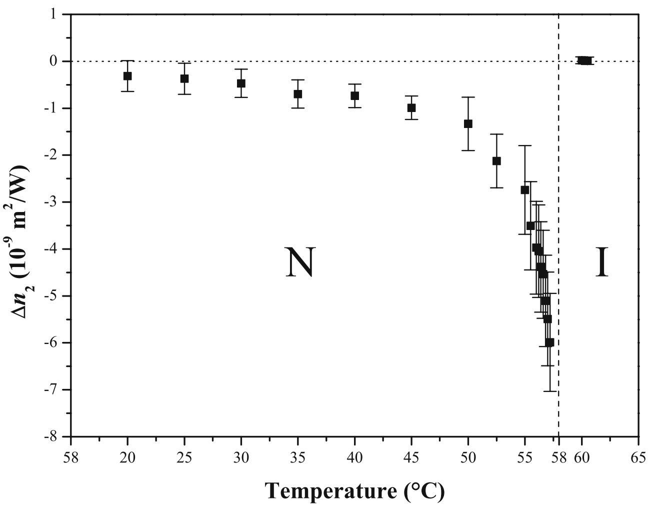

Fig. 5. Nonlinear birefringence as a function of temperature in the nematic phase. The dashed line indicates the clearing temperature.

On the other hand, in the nematic phase and close to the N-I phase transition it is possible to write $S \propto \left(1 - \frac{T}{T^\dagger}\right)^\beta$ [2], where β is the effective critical exponent associated with the order parameter and $T^\dagger$ is the temperature of the effective or virtual second-order transition seeing from below T_{NI} which is different from the spinodal $T^{\star\star}$, representing the absolute limit of the nematic phase on heating, also higher than T_{NI}. So,

$$\Delta n_2 \propto \left[1 - \frac{T}{T^\dagger}\right]^{\beta - 1}. \tag{4}$$

It was observed that for nCB liquid crystals with n=5 to 8, $T^\dagger - T_{\mathrm{NI}} \simeq 0.2\,^\circ\mathrm{C}$ [21]. This difference is of the order of the uncertainness of our measurements of temperature due to both the thermal stage setup and the technique itself (termal lens). Figure 6 shows a ln-ln plot of $|\Delta n_2|$ as a function of the reduced temperature supposing $T^\dagger = T_{\mathrm{NI}}$. To perform the fitting we varied $T^\dagger$ arbitrarily between 58.1 and 58.4°C. A weighted average of these data has given $\beta = 0.28 \pm 0.03$, which is definitely smaller than the mean-field value ($\beta = 0.5$) for a usual critical point (and also smaller than the nonclassical value, $\beta \approx 1/3$), supporting the tricritical scenario of the N-I phase transition. The values of β were always within the calculated uncertainty limits. Of course, the uncertainties to determine β can be attributed to the difficulties to access the virtual second-order transition temperature $T^\dagger$ with a higher precision and to the thermal lens effect itself. Our data is in good agreement with the values obtained by Chirtoc *et al.* [21] ($\beta \simeq 0.24$) for the homologous series nCB ($n = 5$–8) and for 5CB and 6CB obtained by Marinelli *et al.* [22].

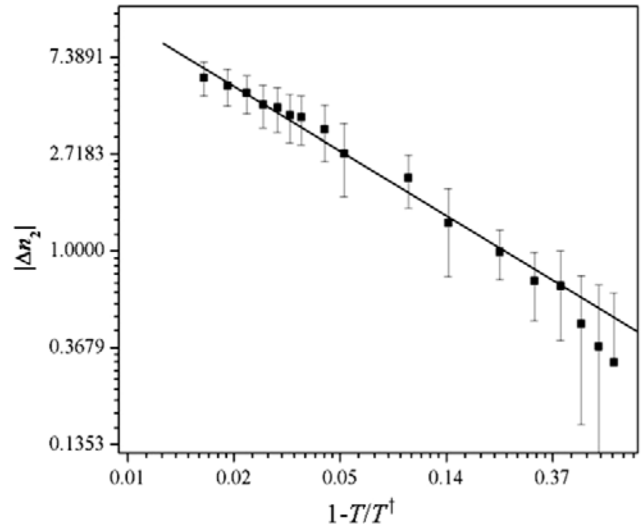

Fig. 6. ln-ln plot of the absolute value of Δn_2 as a function of reduced temperature. Solid line represents a tipical linear fitting of data.

4 Conclusions

We have performed Z-scan experiments to measure nonlinear optical refraction and nonlinear optical absorption properties of the E7 thermotropic liquid crystal mixture in the neighborhood of the nematic-isotropic transition. The data for the nonlinear optical birefringence show a pronounced divergence, which can be associated with an effective critical exponent $\beta = 0.28 \pm 0.03$, and which is thus compatible with the hypothesis of a virtual tricritical point. We also present some statistical-mechanics calculations, for a site-diluted Maier-Saupe model, which provide a justification for the scenario of this virtual tricritical behavior.

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