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In this work, we studied a newly reported class of colossal nonlinear effects observed near the nematic-isotropic temperature transition. We show that the origin of this nonlinearity may be attributed to the onset of critical opalescence. Large diffraction efficiency (23%) and colossal nonlinear refractive index ($n_2 \approx 50\,cm^2/W$) has been measured in randomly oriented thin (1 μm) films of 5CB liquid crystals doped with small quantities of the azo dye methyl red (1%wt).

Keywords: critical opalescence; gratings; methyl red; nematic liquid crystals

INTRODUCTION

The nonlinear optical properties of liquid crystals have been studied intensively over the last two decades. In 1980, Zeldovich *et al.* [1] reported the observation of giant optical nonlinearity ($n_2 = 10^{-5}$ cm^2/W) caused by collective molecular reorientation of the liquid

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crystal, representing at that time the largest nonlinearity ever achieved, and initiating a boom on the study of the nonlinear effects in liquid crystals. Ten years later, Janossy *et al.* [2] noted that nonlinear effect can be enhanced by an additional torque exerted by anthraquinone dyes, obtaining $n_2 = 10^{-3}\,cm^2/W$. Khoo *et al.* [3] reported even larger n_2 values ($1\,cm^2/W$) by doping the liquid crystal 5CB with a small amount of the azo-dye methyl red (MR) [4,5]. This so called supranonlinear effect, was interpreted as a photorefractive-like effect based on the photo-induced space-charge field generated by the spatial modulation of the conductivity and the dielectric anisotropy of the liquid crystal. Last year, Lucchetti et al. [6] obtained a nonlinear refractive index of $\approx 10^3\,cm^2/W$ in randomly-oriented thin liquid crystal cells. The authors named this effect colossal nonlinearity. The origin of the nonlinearity was attributed to surface-induced nonlinear effect, particularly photoadsorption of the dye to the glass substrate, which produced a volumetric reorientation when the anchoring conditions of the dye are affected by light.

Recently, a new class of colossal nonlinear effects has been observed near the nematic-isotropic temperature transition [7]. Very efficient gratings (diffraction efficiency 16%) and colossal nonlinear refractive index ($n_2 \approx 40\,cm^2/W$) has been measured in randomly oriented thin ($1\,\mu m$) films of 5CB liquid crystals doped with small quantities of the azo dye MR (1%wt). However, the origin of the nonlinear effect remains to be elucidated. In this work we show that origin of this nonlinearity may be attributed to the onset of the critical opalescence, i.e., the simultaneous presence of nematic and isotropic phase of liquid crystal near the phase transition.

EXPERIMENT

The experimental setup consists of the usual pump-probe scheme (see Fig. 1). The liquid crystal cell is placed at the intersection of two expanded Ar^+ ion laser beams ($\lambda = 514\,nm$), interfering at an angle of $\alpha = 0.6^\circ$, which correspond to a grating spacing $\Lambda \approx 22\,\mu m$. The power of both beams is equal, so the fringe contrast is maximal. A low power He-Ne laser is used to probe the refractive index change in the cell. The beam diameter the He-Ne laser is chosen to be half of the pump beams. The sample is located inside a home-made oven with optical windows to analyze the behavior of the diffracted beams at different temperatures. Temperature of the oven is controlled by a set of resistor placed symmetrically, to provide homogeneous heating. A thermocouple was placed at different positions inside the oven to

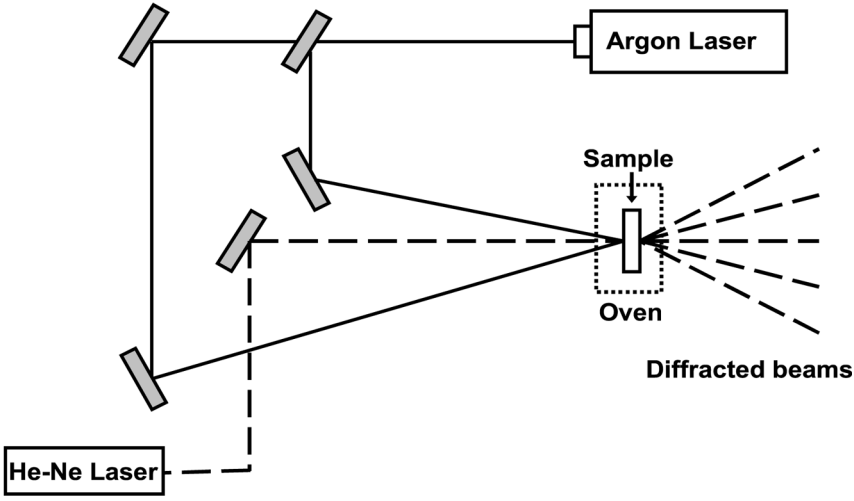

FIGURE 1 Experimental setup to record ($\lambda = 514\,\text{nm}$) and detect ($\lambda = 633\,\text{nm}$) nonlinear gratings. The sample is placed inside a temperature controlled oven.

test the homogeneity of the temperature distribution and it was found to be nearly the same around the sample.

The samples were prepared by sandwiching 5CB liquid crystal (Merck) doped at different concentrations per weight of the azo dye MR (Sigma Aldrich). The glass substrate was cleaned using different solvents to remove organic materials and then placed on an oven to evaporate it completely. Since no surfactants or aligning layers were deposited on the glass substrate, the samples are randomly oriented as reported in Reference [6]. A small droplet of the mixture is placed on one of the substrate and sandwiched by the glass cover. No pressure was exerted, apart from the glass cover own weight, which gives us samples of thickness of approximately $1\,\mu\text{m}$. The sample was sealed with UV curable glue.

RESULTS AND DISCUSSIONS

Figure 2 shows a typical self-diffraction pattern when the sample was heated up to $\approx 33.1^{\circ}\text{C}$ where the diffraction efficiency reaches its peak, as discussed below. The total writing intensity was $I \approx 2\,\text{mW/cm}^2$. Note that 13 orders of diffraction are clearly observed, but we could count up to 20 orders. From the measured diffraction efficiency (23%) at first order (defined as the power at first order divided to

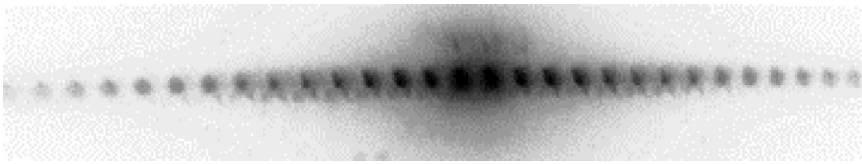

FIGURE 2 Self-diffraction of the writing beams at $T = T_C$. Up 20 diffraction orders could be counted but only 13 are shown. Diffraction efficiency is 23% in 1 μm thick sample.

the incident power) we estimate the nonlinear refractive index as $n_2 \approx 50\,cm^2/W$, which compares well with previous reports [6,7].

In order to study the temperature dependence of the diffraction efficiency, the sample was heat up above the clearing temperature as shown in Figure 3. The clearing temperature T_C, is defined as the temperature at which the scattered light reaches its maximum value. This value of T_C coincides (at least within the resolution limit of our temperature measurements: ~ 0.1°C) with the value obtained by

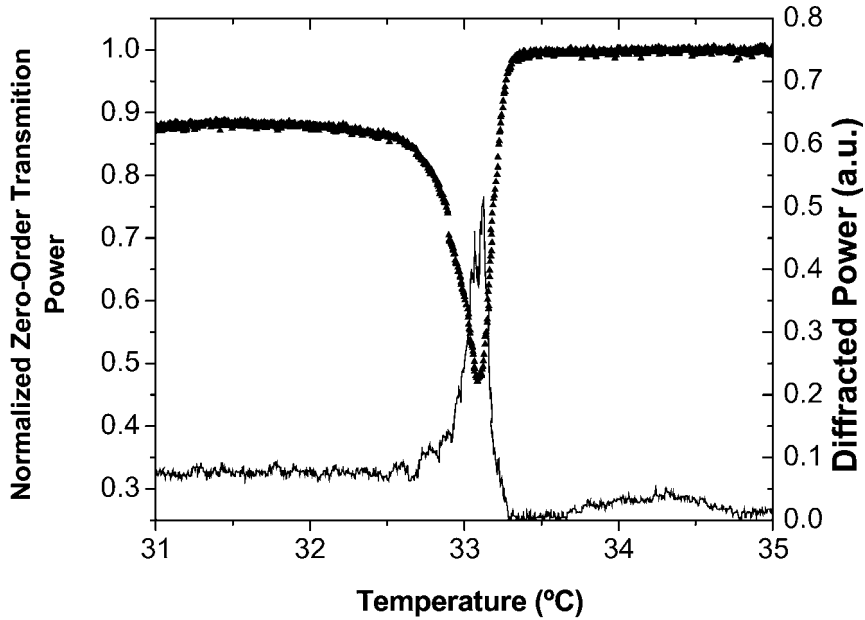

FIGURE 3 Temperature dependence of the zero (filled triangles) and first-order (solid line) diffracted beams for a 5CB liquid crystal doped with 1%wt. of methyl red. Both curves reach their minimum/maximum at the clearing temperature.

measuring the transmission minimum of a sample placed between crossed-polarizers, as reported in Reference [7]. For liquid crystals doped with 1% wt. of MR, the clearing temperature is $T_C = 33.1°C$ meanwhile for pure samples is $T_C = 35°C$. This reduction of T_C in doped samples is accounted for the photoisomerization of methyl red which is known to induce disordering of the nematic phase. Solid line in Figure 3 represents the first-order diffracted signal. It can seen that below $T_C = 33.1°C$ there is a constant temperature-independent grating due to molecular reorientation of the nematic phase (in pure samples such diffracted signal is not seen at the intensity levels used here), then the diffraction efficiency increases rapidly reaching a peak at T_C, and finally decreases very fast until small values at the isotropic phase. We also notice from Figure 3 that the zero-order (filled triangles) is also seriously affected on the same temperature range and follows closely the behavior of the first-order diffracted signal (solid line). The transmitted power is normalized to its value in the isotropic phase where light scattering is minimal. The transmitted zero-order beam power goes from 85% at room temperature to 45% at T_C, however even values as lower as 10% has been measured depending on the measured point. This behavior is qualitatively similar in pure samples of 5CB, but the diffraction efficiency is at least one order of magnitude smaller near T_C, indicating the strong influence that a small amount of dye has on the grating formation of doped samples.

Thus, it seems reasonable to assume that the physical origin of both light scattering and light diffraction must be the same. In order to prove this assumption, we use a 150× magnification nonlinear optical phase contrast microscope illuminated by a He-Ne laser to observe the phase changes inside the sample. The nonlinear phase contrast microscope works in a similar way to a Zernike phase contrast microscope [8] but instead of using fixed phase filters, we used self-aligned photoinduced phase filters. This filter is created when a Kerr nonlinear optical material (bacteriorhodopsin) is placed on the Fourier plane of the objective lens [9]. Figure 4a is a microphotograph just above T_C, where the formation of nematic microspheres immersed in an isotropic phase liquid crystal can be seen. This is characteristic of critical opalescence and it results in very efficient scattering of light [7,10]. The microspheres's size depends on the sample temperature. If T increases from room temperature, their diameter decreases until they disappear leaving only an isotropic liquid crystal phase. Upon cooling from the isotropic phase, they start to pop up from submicron size, increasing as the sample is cooled down; eventually they fuse and form a single nematic domain. The diameters of the microspheres are not uniform as shown in Figure 4a. When the nematic microspheres diameter is

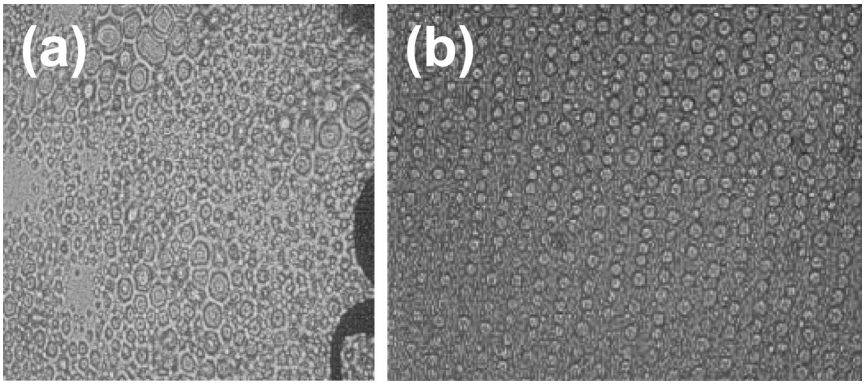

FIGURE 4 Microphotographs were taken using a nonlinear phase contrast microscope with a He-Ne laser as a light source just above T_C (a) when no interference pattern is present and (b) when the interference pattern is turned on.

comparable to the sample thickness ($\approx 1\,\mu m$) then they deform and adapt an approximately cylindrical shape.

The above experiment was repeated with the writing beams on. A narrow bandpass filter was placed in front of the microscope to block the writing beams but not the probe beam. Figure 4b is a microphotography when T is just above T_C. It is clear that the size of nematic microspheres/cylinders is uniform and aligned along the dark interference fringes. This can be easily verified by partially removing the bandpass filter and projecting the image on a screen. The alignment of the nematic microspheres/cylinders along the dark fringes can be easily understood if we recall that methyl red *cis* isomers tend to destabilize the nematic order under illumination with light of adequate energy (methyl red has its absorption peak around 500 nm), i.e., isothermal photoinduced phase transition occur on the bright fringes. Preliminary theoretical studies of the diffraction efficiency produced by an array of symmetrical nematic microcylinders, gives a good qualitatively description of the temperature dependence of the diffraction efficiency. Details of the model will be published elsewhere.

It is commonly believed that pretransitional effects, namely the temperature dependence of the refractive index of the form $(T^* - T)^{-1}$ where T^* is the temperature at which the correlation length becomes infinite; it is responsible for the enhanced nonlinearity when the nematic phase is approached from the isotropic phase [7,11]. However, here we have shown that the diffraction efficiency due to the critical opalescence should be taken into account. More detailed studies are needed in order to fully understand the physical mechanism of

nonlinear refractive index change around the nematic-isotropic phase transition, since many contributions may be present such as thermal indexing, density and volumetric changes [12].

CONCLUSIONS

We have shown that large diffraction efficiency (23%) and colossal nonlinear refractive index ($n_2 \approx 50\,cm^2/W$) has been measured in randomly oriented thin (1 μm) films of 5CB liquid crystals doped with small quantities of the azo dye methyl red (1%wt.) near the nematic-to-isotropic phase transition temperature. We had shown that the origin of this nonlinearity can be attributed to the onset of critical opalescence and pretransitional effects.

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