Investigation of the Soft-Mode Relaxation in a Ferroelectric Liquid Crystal with Picosecond Laser-Induced Dynamic Gratings

R. Macdonald and D. Grebe

Optisches Institut Technische, Universität Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, Germany

(Received 22 October 1992)

The relaxation of light-induced tilt-angle changes in a ferroelectric smectic-C^* liquid crystal is investigated with picosecond laser-induced dynamic gratings. Grating buildup and decay is monitored by diffraction of a cw laser beam. It is shown that reorientation of the liquid-crystal molecules is achieved by rapid optical heating and follows the temperature rise with a characteristic time constant, depending on temperature. The observed rise times correspond to the soft-mode relaxation of the order parameter in a Landau theory describing the smectic-C^*-smectic-A phase transition.

PACS numbers: 61.30.Gd, 42.65.−k, 64.70.Md

Investigations about the influence of light on the orientational order of liquid crystals are of interest for both basic research and applications. Light-induced changes of molecular orientation and alignment can lead, e.g., to optical nonlinear behavior [1] which may be useful for phase conjugation, photonic switching, or optical bistability, but are also of fundamental interest to study the (nonlinear) material response to optical fields. As has been shown previously [2–4], the use of short intense laser pulses offers the unique possibility to investigate different transient phenomena in liquid crystals. It was demonstrated that there is a transfer of energy, linear and angular momentum from the laser pulse to the liquid crystal, exciting fluctuations in temperature, flow processes, and molecular reorientation which change orientational order and the optical properties of the material. The corresponding relaxation processes can be monitored, e.g., with a weak probe beam.

Recently, a new optically induced reorientation effect [5] has been proposed and demonstrated using ferroelectric liquid crystals. Optical axis reorientation of 23 deg has been achieved as a result of optical heating and the temperature dependence of the tilt angle. The effect has been used to realize an optically addressed half-wave plate and opto-optical modulation with low power cw lasers. The switching times of about 1 ms were determined by thermal diffusion in these experiments.

In the present paper we report about investigations concerning the dynamics of light-induced tilt-angle changes in ferroelectric liquid crystals which have been performed with short picosecond laser pulses and the transient grating technique. The investigated tilt-angle relaxation is not only of practical interest for optical switching, but also for fundamental research. Since the tilt angle can be used [6] as an order parameter to describe the smectic-C^*-smectic-A (SmC^*-SmA) phase transition, the presented method allows time-domain investigations of the order parameter relaxation and hence the dynamics of the so-called *soft mode* in ferroelectric liquid crystals. Therefore, the applied dynamic grating technique may be useful in addition to frequency-domain dielectric relaxation measurements [7] which are widely used to study the dynamics of the soft and Goldstone modes in these materials.

The experimental wave-mixing arrangement is sketched in Fig. 1. Two excitation pulses of 80 ps FWHM at $\lambda = 532$ nm are obtained from a frequency-doubled mode-locked Nd-doped yttrium-aluminum-garnet (YAG) laser with a symmetric beam splitter. The two linearly polarized beams are slightly focused to a spot size of about 400 μm diameter with an intersection angle of $\vartheta = 1$ deg onto the liquid-crystal sample. The excitation pulse energy has been about 100 μJ for the following results. The intensity grating resulting from interference of the overlapping beams has a fringe spacing of $\Lambda = \lambda/\sin\vartheta = 30$ μm. A thermal grating is formed by weak absorption of the intensity grating and modulate the optical properties of the thermotropic liquid-crystal film. The center of the induced optical grating is probed by diffraction of a linear polarized weak cw laser beam at $\lambda = 488$ nm on a spot of 100 μm. The first-order diffracted intensity of the probe beam is measured as a function of time with the help of photodiodes and a fast real-time oscilloscope. The temporal resolution was between 200 ps and 2 ns. The polarization of the diffracted light is analyzed with the help of a polarizer placed into

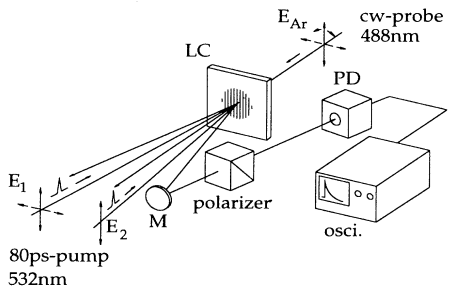

FIG. 1. Experimental arrangement for the investigation of light-induced dynamic gratings with LC, ferroelectric liquid crystal; PD, photodiode; E_1 and E_2, optical excitation fields; E_{Ar}, optical probe field.

the signal beam.

The experiments have been performed with surface stabilized smectic films (ZLI 4237-100 supplied by Merck) of 2 μm thickness in a bookshelflike [8] geometry. A small bias voltage of 9 V is applied across the film via transparent electrodes to additionally stabilize this geometry and to select one of two possible stable molecular orientations. The sample is temperature controlled within ± 0.1 K.

The director (i.e., the axis of preferred molecular alignment) and hence the optical axis is tilted with respect to the smectic layers in the ferroelectric SmC^* phase including an angle Φ with the layer normal axis. The tilt angle Φ is temperature dependent and can be changed by optical heating, leading to optical axis reorientation [5]. The response to a short excitation pulse in a dynamic grating experiment obtained with the SmC^* and the SmA phase of a ferroelectric liquid crystal is shown in Fig. 2, where the square root of the diffracted probe beam is displayed as a function of time on a microsecond time scale. The δ-peak-like excitation takes place at $t=0$ in the graphs. The square root of the signal is proportional to the optical grating amplitude [9] in the weak grating approximation and thus displays the dynamics of the induced birefringence changes. The weak grating approximation is valid here because the diffraction efficiency was in the range of 1% and less in these experiments.

The undisturbed director was always adjusted to be parallel to the incident probe beam polarization. The curves denoted with $\perp$ and $\parallel$ in Fig. 2 correspond to the depolarized and the parallel-polarized diffracted signal with respect to the incident polarization. Since the birefringence and the film thickness of the samples are matched to provide that $(n_\parallel - n_\perp)d \approx \lambda/2$, the square root of the depolarized signal is proportional to the induced optical axis rotation and thus proportional to the tilt-angle changes.

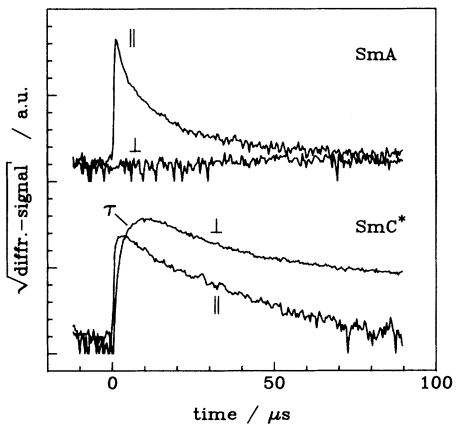

FIG. 2. Square root of the diffracted probe beam intensity vs time after ps grating excitation obtained with the SmA and SmC^* phases of a ferroelectric liquid crystal, $|T-T_c|=5$ K. Excitation energy is $W_p=100$ μJ. The index $\perp$ ($\parallel$) corresponds to the depolarized (parallel-polarized) signal with respect to the incident probe beam polarization.

No depolarized signal has been observed in the SmA phase (see Fig. 2) because the electrical-field-induced tilt of the molecules is rather small, and the discussed reorientation effect was not proved. The signal shown for the SmA phase was parallel polarized with respect to the incident probe beam polarization and directly displays the dynamics of the induced thermal grating. The temperature modulation mainly affects the optical properties via density changes in this case and relaxation of the density is much faster than thermal grating decay [9] which is determined by heat diffusion, running on a microsecond time scale.

Clearly, there is a strong depolarized signal in the SmC^* phase, showing a much slower increase and rise times of a few microseconds or less. This depolarized signal is a strong indication that the discussed director reorientation is excited in the experiments. There is also a parallel-polarized signal contribution in this phase, which contains fast density modulations as observed in the SmA phase, plus an additionally weak component due to the axis reorientation. The signal decay is given by microsecond thermal grating relaxation and an additionally slower millisecond component which can be attributed to the relaxation of elastic deformations in the SmC^* phase as will be discussed below. It must be noted, however, that for stronger excitation energies (>100 μJ) severe distortions and eraseable permanent gratings have been observed, which has also been reported [3] by other authors.

The rise times of the depolarized signal obtained in the SmC^* phase correspond to the tilt angle relaxation and hence to the soft-mode relaxation as will be discussed below. They are temperature dependent and range from 0.7 to 5 μs as can be seen in Fig. 3.

The experimentally investigated order parameter relaxation and the observed temperature dependence of the

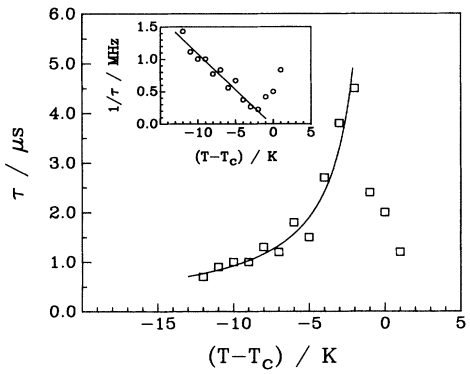

FIG. 3. Temperature dependence of the evaluated soft-mode relaxation times. T_c is the SmA-SmC^* phase transition temperature. The inset shows the reciprocal relaxation times vs temperature.

grating rise times can be described by a dynamic equation for the tilt angle Φ which can be written in a relaxation time approximation as [10,11]

$$\tau_0 \frac{\partial \Phi}{\partial t} + (NkT)^{-1} \frac{\partial g}{\partial \Phi} = 0 , \quad (1)$$

where τ_0 is a "naked" relaxation time, N the number density of molecules, k the Boltzmann constant, T the temperature, and g the free energy density. We assume a Landau-type potential for the free energy where the tilt angle is used as the amplitude of a primary order parameter to describe the (steady state) transition from the low temperature SmC^* phase of reduced symmetry to the symmetric high temperature SmA phase, which was first suggested by Pikin and Indenbom [12] and has been subsequently refined by several authors. Flow and flow-alignment effects are neglected in writing Eq. (1). In most ferroelectric liquid crystals the SmC^*-SmA phase transition is found to be of second order [6,12], except in some materials with very large spontaneous polarization, where it is of weak first order [13]. It is assumed here that the investigated transition is of second order and g can be written as

$$g = g_0 + \frac{1}{2} A \Phi^2 + \frac{1}{4} B \Phi^4 + \frac{P^2}{2\varepsilon_0 \chi} - \kappa P \Phi , \quad (2)$$

where $A = A_0(T - T_0)$, P is the spontaneous polarization, and χ is the dielectric susceptibility. A_0, B, and κ are constants. The free energy of the high temperature phase $T > T_0$ corresponding to $\Phi = 0$ is denoted by g_0. Terms considering the helical winding of the SmC^* phase, the elastic free energy, the flexoelectric effect, and higher order correction terms [6] are neglected in Eq. (2) since their contributions to the free energy are rather small well below the transition temperature. Further, it was found that the observed relaxation times do not depend upon the applied dc electric field, in agreement with previous results [7] obtained in dielectric relaxation measurements. As a consequence, the dipole energy of the spontaneous polarization in external electric fields is omitted from Eq. (2).

The last term of the Landau potential (2) describes a linear coupling between the spontaneous polarization P and the tilt angle Φ. It should be noted at this point that the spontaneous polarization in ferroelectric liquid crystals is not driving the phase transition but is a secondary parameter as a result of the reduced symmetry of chiral smectic-C phases (so-called "improper" ferroelectrics).

The steady state tilt angle can be calculated by minimizing the free energy to give $\Phi_{eq} = [A_0(T_c - T)/B]^{1/2}$, where $T_c = T_0 + \varepsilon_0 \chi \kappa^2 / 2A_0$ is the phase transition temperature, which is slightly shifted due to the coupling between P and Φ with respect to the transition temperature T_0 without coupling.

Inserting the free energy (2) into Eq. (1) gives a nonlinear relaxation equation for the tilt angle

$$\gamma \frac{\partial \Phi}{\partial t} + A_0(T - T_c)\Phi + B\Phi^3 = 0 , \quad (3)$$

where $\gamma = \tau_0 NkT$ has the dimension of viscosity. Assuming a small light-induced perturbation in temperature and the equilibrium tilt angle, i.e., $T = T_{eq} + \bar{T}(t)$ and $\Phi = \Phi_{eq} + \bar{\Phi}(t)$ with $\bar{T} \ll T_{eq}$ and $\bar{\Phi} \ll \Phi_{eq}$, allows linearization of Eq. (3) by neglecting terms with $(\bar{T}\bar{\Phi})$, $\bar{\Phi}^2$, and $\bar{\Phi}^3$ which results in

$$\gamma \frac{\partial \bar{\Phi}}{\partial t} + 2A_0(T_c - T_{eq})\bar{\Phi} = -A_0 \Phi_{eq} \bar{T} . \quad (4)$$

For constant temperatures ($\bar{T} = 0$) Eq. (4) describes an exponential relaxation of the order parameter perturbation towards the equilibrium value. The corresponding relaxation time is temperature dependent and given by

$$\tau = \frac{\gamma}{2A_0(T_c - T_{eq})} \quad \text{for } T_{eq} < T_c . \quad (5)$$

If now a light-induced temperature increase $\bar{T}(t)$ is considered, which is due to absorption of the short laser pulse and optical heating, the perturbation $\bar{\Phi}(t)$ is driven by the right-hand side of Eq. (4) and solutions are given by the convolution

$$\bar{\Phi}(t) = -A_0 \Phi_{eq} \gamma^{-1} \int_{-\infty}^{t} \bar{T}(t') \exp\left\{ -\frac{t - t'}{\tau} \right\} dt' . \quad (6)$$

The dynamics of the temperature increase can be calculated [9,14] with the heat diffusion equation, which in the present case approximately gives $\bar{T} = \bar{T}_0 \exp\{-t/\tau_w\}$ for $t \geq 0$, where τ_w is the thermal grating relaxation time. As discussed above, this thermal grating relaxation is displayed in Fig. 2 by the signal obtained with the SmA phase and τ_w is in the range of several ten microseconds. Integration of Eq. (6) then yields

$$\bar{\Phi}(t) = \bar{\Phi}_0 (\exp\{-t/\tau_w\} - \exp\{-t/\tau\}) , \quad (7)$$

where $\bar{\Phi}_0 = -A_0 \Phi_{eq} \gamma^{-1} \tau \tau_w (\tau_w - \tau)^{-1}$, which is negative because an increase in temperature decreases the tilt angle.

According to Eq. (7) the tilt angle follows the rapidly increased temperature with the time constant τ, Eq. (5), which is the same as for constant temperatures in the small perturbation approximation. The relaxation is a result of molecular reorientation and hence determined by the viscosity γ. The reorientation relaxation is observed as the grating buildup if $\tau_w > \tau$ and the rise times of the depolarized signal directly display the order parameter dynamics as discussed above. The induced tilt-angle changes can be estimated from the observed diffraction efficiencies of, e.g., 0.5% (at $W_p = 100$ μJ) to $\bar{\Phi} = 2$ deg, which corresponds to a laser-induced temperature rise of about 1 K. This temperature rise is in agreement with thermal grating calculations assuming a nonlinear absorption coefficient as observed recently [14] in cyanobiphenyl molecules.

The observed temperature dependence of τ, which has been evaluated by fitting Eq. (7) to the experimental data, agrees very well with the theoretical expression (5) for temperatures not too close to the transition, confirming that the observed effects are due to laser-induced tilt-angle changes. The viscosity γ connected with the soft-mode relaxation can be estimated with Eq. (5) from experimental data to $\gamma=0.25$ kg m^{-1}s^{-1}, assuming [10,15] that $2A_0=kN$. This is close to the value $\gamma'=0.34$ kg m^{-1}s^{-1} given by Merck for the rotational viscosity.

The deviations between calculated and experimentally observed soft-mode relaxation times in the vicinity of the phase transition may indicate the limits of the used model and approximations. In particular, the small perturbation approximation is no longer valid near T_c. Furthermore it is well known that spontaneous fluctuations in the order parameter are increasing dramatically near the phase transition, which is not considered in a phenomenological Landau theory. As a result, the amplitudes of the signal corresponding to the distinctively excited soft mode are very small close to T_c and were hard to distinguish from the relaxation of spontaneous fluctuations. The evaluated relaxation times are therefore much less certain than those obtained well below the transition.

The signal decay as described by Eq. (7) is determined by thermal grating relaxation and heat diffusion mainly, which in the present experiments is clearly slower than the order parameter relaxation. As a consequence, the order parameter is almost in equilibrium with the decreasing temperature and τ cannot be determined from grating decay. The additionally observed slower millisecond grating decay times can be explained by the relaxation of elastic deformations which are a result of the optothermal reorientation process. The time constant for the relaxation of elastic director deformations is given [1-4] by $\tau_r=\gamma' d^2/\pi^2 K$ and can be calculated to $\tau_r=15$ ms using parameters like $\gamma'=0.34$ kg m^{-1}s^{-1}, $K=5.25\times10^{-12}$ N, and $d=2$ μm in good agreement with the experimental data.

In conclusion, the dynamics of laser-induced reorientation effects in a ferroelectric liquid crystal have been investigated in transient grating experiments using picosecond excitation pulses. Reorientation in the SmC^* phase has been achieved by rapid optical heating as a result of weak absorption of the short excitation pulse and the temperature dependence of the tilt angle. It is shown that the tilt angle follows the fast temperature rise with the soft-mode relaxation time which range between 0.7 and 5 μs for the investigated ferroelectric liquid crystal, depending on temperature. The following grating decay is determined mainly by heat diffusion out of the rather thin liquid-crystal film via the surfaces of the glass container and takes several tens of microseconds. Additionally, relaxation of elastic deformations resulting from thermally induced molecular reorientation has been observed as the SmC^* phase with decay times of 15 ms.

The observed soft-mode relaxation has been explained with a dynamic model of second-order phase transitions and the calculated relaxation times are in good agreement with experimental data if the introduced viscosity connected with the soft-mode dynamics is in the range of $\gamma=0.25$ kg m^{-1}s^{-1}. The theoretical temperature dependence of the relaxation time is in very good agreement with experimental observations for temperatures not too close to the phase transition.

Financial support from the Deutsche Forschungsgemeinschaft via the Sonderforschungsbereich "Anisotrope Fluide" is gratefully acknowledged. Excellent SSFLC cells have been supplied by L. Kiesewetter and M. Haussmann (Institute of Precision Mechanics TU Berlin). Finally, we would like to thank H. J. Eichler (TU Berlin) for very helpful and stimulating discussions.

[1] I. C. Khoo, in *Progress in Optics: Nonlinear Optics of Liquid Crystals*, edited by E. Wolf (North-Holland, Amsterdam, 1986).
[2] H. Hsiung, L. P. Shi, and Y. R. Shen, Phys. Rev. A **30**, 1453 (1984).
[3] I. C. Khoo, R. G. Lindquist, R. R. Michael, R. J. Mansfield, and P. LoPresti, J. Appl. Phys. **69**, 3853 (1991).
[4] H. J. Eichler and R. Macdonald, Phys. Rev. Lett. **67**, 2666 (1991).
[5] R. Macdonald, J. Schwartz, and H. J. Eichler, Int. J. Nonlinear Opt. Phys. **1**, 103 (1992).
[6] R. Blinc, C. Filipic, A. Levstik, B. Zeks, and T. Carlsson, Mol. Cryst. Liq. Cryst. **152**, 503 (1987).
[7] S. U. Vallerien, F. Kremer, H. Kapitza, R. Zentel, and W. Frank, Phys. Lett. A **138**, 219 (1989).
[8] N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett. **36**, 899 (1980).
[9] H. J. Eichler, D. Günter, and D. W. Pohl, in *Laser-Induced Dynamic Gratings*, edited by T. Tamir (Springer, New York, 1986).
[10] S. Hess, Z. Naturforsch. **30a**, 728 (1975).
[11] S. R. DeGroot and P. Mazur, in *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
[12] S. A. Pikin and V. L. Indenbom, Usp. Fiz. Nauk **125**, 251 (1978) [Sov. Phys. Usp. **21**, 487 (1978)].
[13] B. R. Ratna, R. Shashidhar, Geetha. G. Nair, S. Krishna Prasad, Ch. Bahr, and G. Heppke, Phys. Rev. A **37**, 1824 (1988).
[14] H. J. Eichler, R. Macdonald, and B. Trösken, Mol. Cryst. Liq. Cryst. (to be published).
[15] P. A. Madden, F. C. Saunders, and A. M. Scott, IEEE J. Quantum Electron. **22**, 1287 (1986).