Ferroelectric phase transitions and electroclinic effect in thin cells of chiral smectic liquid crystals.

Yu G. Fokin, T.V. Murzina, O.A. Aktsipetrov

Department of Physics, Moscow State University, 119992 Moscow, Russia.
aktsip@shg.ru

S. Soria

Institut de Ciencies Fotoniques, Jordi Girona 29, Edifici Nexus II, 08034 Barcelona, Spain

G. Marowsky

Laser Laboratorium Goettingen e.V., Hans-Adolf-Krebs-Weg 1, D-37077 Goettingen, Germany

Short Abstract
Ferroelectric smectic C* (SmC*) – smectic A* (SmA*) phase transitions and electroclinic effect (EC) in micron-size cells of chiral liquid crystals (LC) are studied by second harmonic generation (SHG) technique. SHG is a well-known method for probing ferroelectric phase transitions due to its high sensitivity to the polar state and symmetry changes of the matter [1]. Quadratic non-linear polarisation in ferroelectric LC is proportional to the spontaneous polarisation, which exists in thin LC cells with unwounded helix. Critical behaviour of spontaneous polarisation follows that of the tilt angle, which is an order parameter of SmC*-SmA* phase transition in LC. Temperature dependencies of the SHG intensity are studied for biased and unbiased LC cells and reveal a second order SmC*-SmA* phase transition and EC effect. Reflected and transmitted SHG are studied to distinguish between non-linear responses from the sub-surface and bulk layers of the LC. The analysis of temperature dependencies shows a strong surface coupling resulting in the existence of the DC electric field and temperature independent unswitchable "frozen" subsurface layer. Critical exponents are determined from the SHG temperature dependencies in the vicinity of the transition point and conform the superfluid model.

Keywords
Liquid crystals, second harmonic generation, electroclinic effect, ferroelectric phase transitions.

Introduction
Ferroelectrically ordered SmC* phase of chiral LC is characterised by a non-zero tilt angle of the molecular long axes out from the layer normal, which is an order parameter of the SmC*-SmA* phase transition. The critical exponent below the transition temperature either reveals a classical Landau behaviour, or follows an analogy with the superfluid helium, predicted by de Gennes [2]. The critical behaviour of the order parameter is also not studied well in the region above the phase transition in the SmA* phase, where the EC effect can occur [3]. EC effect consist of the molecular director tilt out of the layer normal and orthogonal to the applied DC electric field in the SmA* phase. Then the non-zero tilt angle appears and diverges near the transition point. In thin LC cells ferroelectric properties of the bulk and sub-surface layers are strongly influenced by the interaction of the interfacial layers with the substrate. Various treatments of the inner cell surfaces influences on LC layers packing, type of ferroelectric switching and critical behaviour of the order parameter near the transition point, which has a great practical importance for LC-based devices technology. In this paper we investigate the

critical behaviour of the chiral LC cells in the vicinity of the SmC*-SmA* phase transition by means of optical SHG technique. The main emphasis is made on the comparison of the reflection and transmission geometries. In transmission the whole cell participates in SHG, while in reflection the coherence length for SHG is much smaller, which allows to distinguish between non-linear responses from the bulk and sub-surface layers of the LC cell.

Experimental or Computational details

Experimental setup and samples preparation are described elsewhere [4]. Briefly, SmC* phase of the LC is achieved by a slow cooling of a LC mixture from the isotropic phase, deposited capillary into the thin cell of 2 micron thickness. The critical temperature of SmC*-SmA* transition of the mixture used is ~ 42^{o}C. Thin indium-titanate oxide electrodes are evaporated on the inner sides of the cells and then covered by a polymer layer. Anisotropic interaction of the polymer with the sub-surface layers of the cells results in the orientation of the LC layers with the direction of the C_2 symmetry axes being parallel to the polymer treatment direction. Experimental setup consists of an OPO laser system with the fundamental wavelength of 537 nm and pulse duration 15 ns. Photomultiplier tube and gated electronics contain the registration system. Temperature dependencies of the SHG intensity are measured in the range from 20 to 55^{o}C, in the absence and presence of the DC electric field varied from 0 to ±10 MV/m, and in reflection and transmission geometries with angles of incidence of 45 and 0 (normal incidence) degrees, respectively.

Results and discussion

Usually in the bulk of the sample LC layers tend to form helicoidal structure which leads to the compensation of the spontaneous polarisation, though a single chiral LC molecule can have non-zero dipole moment due to the symmetry considerations [5]. Embedding the LC into the thin cell results in the helix unwinding and spontaneous polarisation appears. Then the temperature dependence of the net dipole moment of the cell follows that of an order parameter of the transition, the tilt angle, in the critical region. SHG intensity is proportional to the squared non-linear polarisation, which, in turn, is determined by the spontaneous polarisation of ferroelectric LC. Thus, analysis of SHG temperature dependencies allows to obtain an order parameter behaviour in the vicinity of the phase transition. On fig. 1a the SHG temperature dependencies are shown for biased and unbiased LC cells in transmission geometry at normal incidence. The characteristic critical behaviour is obtained in the vicinity of the transition point. The hysteresis-free character of the dependencies justifies the second order of the phase transition. To explain the observed dependencies, the interference of the electric field and temperature dependent and independent contributions is suggested. Comparative analysis of the reflection and transmission geometries shows the existence of several sub-surface “frozen” layers, stabilised by a strong surface coupling, which do not respond neither to application of the electric field nor to temperature variations. For qualitative comparison of the non-linear responses in reflection and transmission geometries, the contrast K of the dependencies is introduced, determined by the ratio of the difference and the sum of the SHG intensity square roots for opposite biasing – fig. 1b.

$$K = \frac{\sqrt{I_{2\omega}(+E)} - \sqrt{I_{2\omega}(-E)}}{\sqrt{I_{2\omega}(+E)} + \sqrt{I_{2\omega}(-E)}} \quad , \qquad (1)$$

where $I_{2\omega}(\pm E)$ is the SHG intensity from biased and unbiased cells.

Under the assumption of the equality of absolute values of the non-linear polarisation corresponding to opposite applied electric fields $P_{NL}(+E) = P_{NL}(-E)$, the amplitude of the contrast is determined by the ratio of field dependent $P_{NL}(E)$ and independent P_{const} contributions to SHG, and power law of the temperature T:

$$K \sim \begin{cases} \dfrac{P_{NL}(E)}{P_{const}}\left(1-\dfrac{T}{T_c}\right)^{\beta}, T < T_c \\ \dfrac{P_{NL}(E)}{P_{const}}\left(1-\dfrac{T}{T_c}\right)^{-\gamma}, T > T_c \end{cases}, \quad (2)$$

where T_c is temperature of the phase transition, and β and γ are critical exponents. The contrast is bigger in transmission, as in this case the coherence length for the SHG and thus, electric field dependent contribution, are larger than in reflection, in agreement with the suggested model. The presence of a non-zero polarisation in SmA* phase and its divergence near the transition point indicates the existence of EC effect. The critical exponents below and above the temperature of the SmC*-SmA* phase transition are 0.31 and 1.4, respectively, corresponding to the superfluid helium model.

Conclusions

SmC*-SmA* phase transitions and EC effect have been studied in thin planar cells of ferroelectric chiral LC by means of SHG technique. The analysis of the temperature dependencies of non-linear quadratic response in the critical region leads to the assumption of a strong surface coupling, resulting in the stabilisation of several "frozen" sub-surface twisted layers, independent on electric field and temperature. Critical exponents in the vicinity of SmC*-SmA* phase transition reveal a behaviour, characteristic to the superfluid helium theory.

Acknowledgements

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Figures and Tables

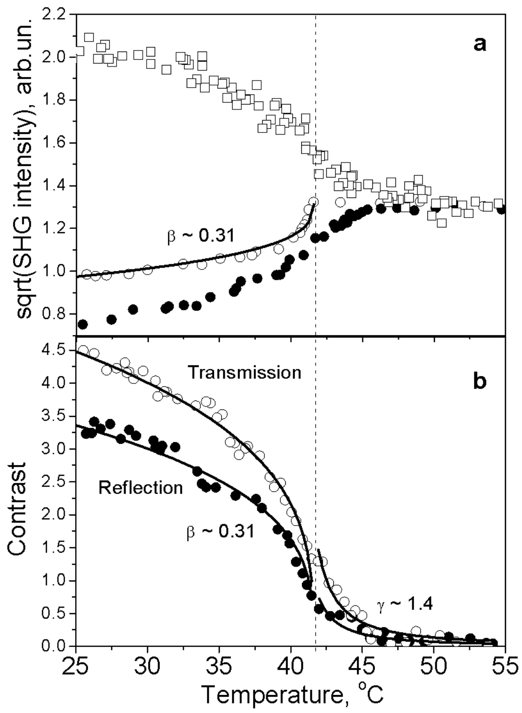

Fig 1a: Temperature dependencies of square root of SHG intensity in the absence of the electric field (open circles), at field +8MV/m (squares) and –8MV/m (filled circles). Solid line is theoretical fit.

Fig 1.b: Temperature dependencies of the contrast in reflection (filled circles) and transmission (open circles) geometries. Solid lines are theoretical fit by (2).