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Determination of bulk values of twist elasticity coefficient in a chiral smectic C* liquid crystal

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A method is described for determination of bulk values of a twist elastic coefficient for smectic c-director in chiral smectic liquid crystals with a helical structure. The method was applied to 4-methylbutyloxy phenyl-4-octyloxy-benzoate (C8) in the chiral smectic C* phase. The measurements were performed using optical detection in a small deformation limit. In contrast to the usual methods, initial deformation of the helix (caused by strong surface interactions) was avoided by using homeotropic aligned thick samples. The critical temperature dependence of the measured coefficient was observed. The relation between the measured parameter and the smectic C order parameter is presented.

Keywords: ferroelectric liquid crystals, smectic, twist elasticity coefficient.

1. Introduction

Significant research in the field of liquid crystals has been directed towards characterizing the structure of the chiral smectic phases. These phases have proven to be of theoretical importance because they provide ferroelectric (smectic-C*), antiferroelectric (smectic-C_a*), or ferrielectric behaviour in samples without 3D long-range positional order. The chiral smectic phases also have large technological importance in fast electro-optic switching devices [1,2] including high definition TV screens and computer monitors.

The switching time of ferroelectric liquid crystals depends on the value of spontaneous polarization and on mechanical properties. The sensitivity of the liquid crysta1 cell on various external factors and the value of the switching threshold depends on elastic coefficients, first of all on the twist elastic constant for the **c** director B_3 (according to the notation of de Gennes [3], used also by Dahl and Lagerwall [4]). Therefore determination of this parameter is of large technical value. Despite their great importance, the experimental data concerning the elasticity coefficients are rather scarce and often contradictory, mostly due to incorrect measuring procedures. For correct measurement of any elastic coefficient, the condition of small deformation must be fulfilled. The condition of small deformation can be easily fulfilled in the case of dielectric [5–9], electrooptic [10–12], pyroelectric [13] or light scattering [14] experiments. These experiments are, however (with only a few exceptions [10,15,16]) being performed for planar aligned samples or free standing films [11,17], which are either helix-free or possess strongly deformed helical structure. Up to now, me-chanical properties of the **c**-director in ferroelectric smectics with non-deformed or weakly-deformed helical structure have rarely been investigated [16,18].

Here, we propose a method for determination of the twist elastic coefficient B_3 for the smectic **c**-director. This method fulfils the condition of small deformation. Moreover, the measurement was performed with homeotropic oriented samples, in which the helix is much less deformed than in usually used planar samples.

2. Principle of measurement

In order to measure any elastic coefficient, one has to apply an appropriate stress to the properly oriented sample and measure the deformation caused by this stress. Both the stress and deformation have to be small to fulfil the condition of proportionality between deformation and stress (Hook's law). In the case of chiral smectics C, it means that the change in the angle between **c**-directors in the neighbouring smectic layers must be small in comparison to the equilibrium value of this angle.

The simplest way to introduce a deformation is by applying an electric field parallel to the smectic layers [19–21]. The electric field couples to the smectic layer dipoles of the helical smectic C* phase and, with increasing field, twists those dipoles which are not already lined up with the field. This means that the field will introduce a macroscopic polarization of the medium and finally removed the helix completely. In that case, the condition of small deformation means that the electric field strength has to be much lower than the critical field E_C needed for unwinding the helix.

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Tilted smectic liquid crystals have low symmetry and for this reason many elastic coefficients [4] are needed to describe their properties. In this paper we limited ourselves to determination of the twist elastic constant B_3 (according to the notation of Ref. 4) for the smectic **c**-director, i.e., the projection of the nematic **n**-director on the layer plane [3]. As mentioned before, this coefficient strongly affects the properties of displays based on ferroelectric liquid crystals.

The method of detection of the deformation creates a separate problem. Deformation of the molecular distribution causes a change in the macroscopic properties of the sample. The optical properties are relatively easy to detect and we used them for detection of deformation. For numerical estimation of B_3, it is necessary to assume models connecting both the deformation of molecular distribution with the strength of electric field and the molecular distribution with the macroscopic optical properties of the sample.

2. Theory

In an ideal nondisturbed chiral smectic C, the position of **c**-director in the successive smectic layers is described by

$$\varphi = \frac{2\pi \cdot z}{p}, \qquad (1)$$

where φ is the azimuthal angle between **c**-director and the arbitrarily chosen x-axis of the Cartesian coordinate frame, z is the coordinate in the direction normal to the smectic layers whereas p is the pitch of the helix.

After applying an electric field parallel to the smectic layers, the effective dipole moment of the smectic layers tends to reorient in the electric field direction. This reorientation is hindered by elastic and viscosity forces. Because the properties of **c**-director are similar to the properties of the nematic **n**-director, we can use the nematodynamic equation for description of the azimuthal angle φ [3,22]. At sufficiently low frequency of the external electric field, the equation of motion takes a simple form

$$-B_3 \frac{\partial^2 \varphi}{\partial z^2} = P_S \cdot E \sin \varphi, \qquad (2)$$

where P_S is the spontaneous polarization and $E = E_0 \cos \omega t$ denotes the strength of the electric field of the angular frequency ω applied to the sample. In the case of small deformations, the steady state solution of Eq. (2) reads [22]

$$\varphi = qz + \varphi_0 \cdot \cos \omega t \cdot \sin qz, \qquad (3)$$

where $q = 2\pi/p$ and φ_0 is the amplitude of φ-angle change

$$\varphi_0 = \frac{P_S \cdot E_0}{B_3 q^2}. \qquad (4)$$

The second term in Eq. (3) describes the response of the chiral smectic C* to the applied AC electric field. The changes in φ-angle are also periodic with the same angular frequency as the external field.

The helix deformation described by Eq. (4) causes the changes in dielectric and optical properties of the chiral smectic C*. One of the easy detectable changes is the inclination of the optical axis. When the molecular tilt angle θ is small, the relation between the azimuthal angle amplitude φ_0 and the optic axis inclination amplitude ϑ_0 has the following approximate form [22]

$$\vartheta_0 = \frac{1}{2} \varphi_0 \cdot \theta. \qquad (5)$$

Thus, the measurement of the optical axis inclination amplitude at low frequencies enables to determine B_3 using Eqs. (4) and (5)

$$B_3 = \frac{P_S \cdot E_0 \cdot \theta}{2\vartheta_0 \cdot q^2}. \qquad (6)$$

3. Experimental

We have examined the SmC* phase of 4'-methylbutyloxy phenyl-4-octyloxy-benzoate (abbreviated here C8). This material exhibits the following scheme of phase transitions

Cryst 48°C (SmIV 12°C SmIII 21°C SmC* 43.1°C) SmA 59°C Iso

where SmIII and SmIV stand for some highly-ordered smectic phases.

For determination of the elastic constant, three different experiments were necessary. In the first step, the spontaneous polarization P_S was measured with the Diamant--Pepinsky bridge [23]. This measurement demands a homogeneously aligned sample. This was achieved by slowly cooling the liquid crystal sample from the isotropic to the SmA phase. In this way we obtained a homogeneous orientation of smectic layers perpendicularly to the electrode. The semitransparent ITO (indium tin oxide) electrodes separated by 30-μm spacer were unidirectionally rubbed. The orientation of the sample was checked with the polarizing microscope. The sample temperature was controlled by the Mettler FP5 temperature controller within ±0.1 K.

In the second step, the pitch of the helix p was measured in homeotropically aligned samples using two methods, the spectroscopic one (in the temperature region 34–40.5°C) and the Cano method in wedged sample (from 33°C up to the Smectic C* – Smectic A phase transition). Both methods give the same results, for the refractive index of the ordinary ray equal to 1.4. The results are presented in Fig. 2.

It is worth to notice that the diffraction method applied for the same material in planar orientation gave different results. The difference is probably caused by the influence of surfaces in the case of planar oriented samples used for diffraction measurements. This problem will be discussed elsewhere [24].

In the next step we measured the amplitude of inclination angle of the optical axis ϑ and the tilt angle θ in homeotropically oriented samples. The samples were ori-
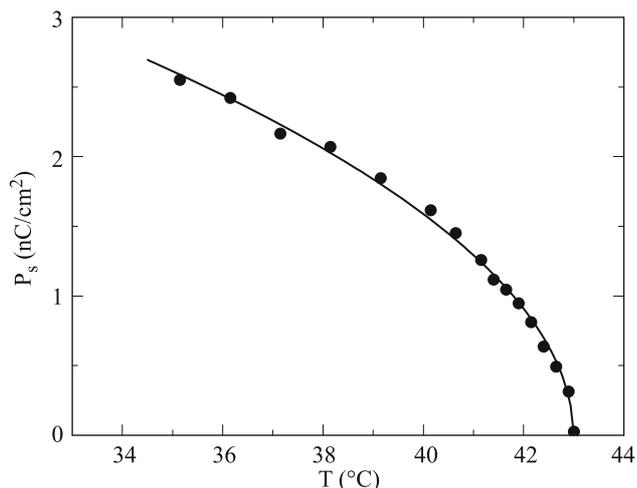
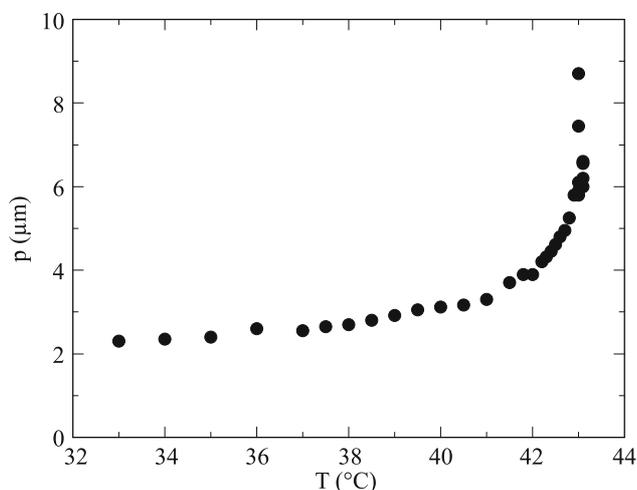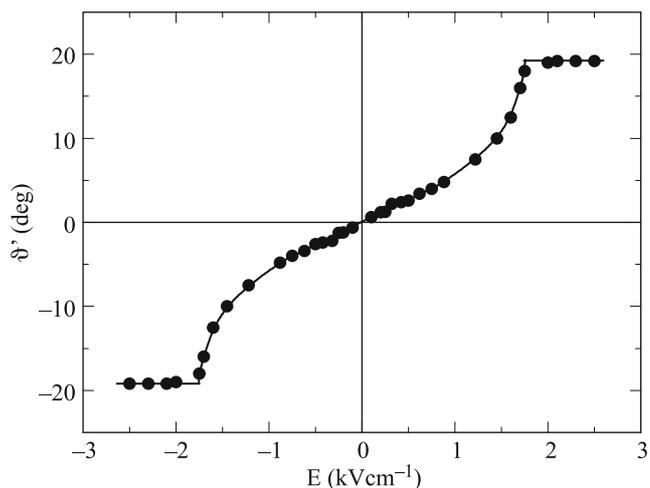Fig. 1. Temperature dependence of spontaneous polarization.

Fig. 3. Dependence of apparent optic axis inclination on electric field strength at $T = 41°C$.

From plots like that in Fig. 3 we determine the slope for $E = 0$, needed for the calculation of B_3. The temperature dependence of $d\vartheta'/dE$ obtained for DC field is shown in Fig. 4. The temperature dependence of θ' is plotted in Fig. 5.

We observed the inclination of optical axis caused by electric field also in the SmA phase. This electroclinic effect [25] fulfils the Curie-Weiss law, $d\vartheta'/dE \propto 1/(T - T^*)$, where T^* is equal to T_{CA} within the limits of the experimental error (± 0.1 K).

The measurements of the inclination angle as a function of frequency showed that this angle does not depend on frequency below 5 Hz.

4. Discussion

The experimental results presented in the former section were used to calculate the twist elastic constant B_3 from Eq. (6). The temperature dependence of this parameter is given in Fig. 6.

Fig. 2. Temperature dependence of helical pitch.

ented in the SmA phase using a surfactant (Quilon C). Two aluminium 110-μm thick electrodes were glued on one glass plate in a distance of 1.6 mm. The electric field was directed in the smectic layers plane.

After applying the electric field we observed, in both the SmC* and the SmA phase, the inclination of the optical axis of the sample in a plane perpendicular to the field direction. The observation was made using conoscopic technique. In small field strength limit, the inclination of the optic axis was proportional to the field (Fig. 3). At higher field strengths, the dependence $\vartheta(E)$ became nonlinear up to the critical field unwinding the helix. At E_C, the optical axis inclination became equal to the molecular tilt θ.

The angle ϑ' shown in Fig. 3 was measured outside the sample ($\sin \vartheta' = n' \cdot \sin \vartheta$, where n' is the refractive index in the direction of observation). Similarly, the value of the apparent tilt angle θ' obtained from Fig. 3 is n'' times larger than the tilt angle ($\theta' = n''\theta$, where n'' is the refractive index in the tilt direction). Because θ is small, we can assume that both n' and n'' are equal to the ordinary refractive index n.
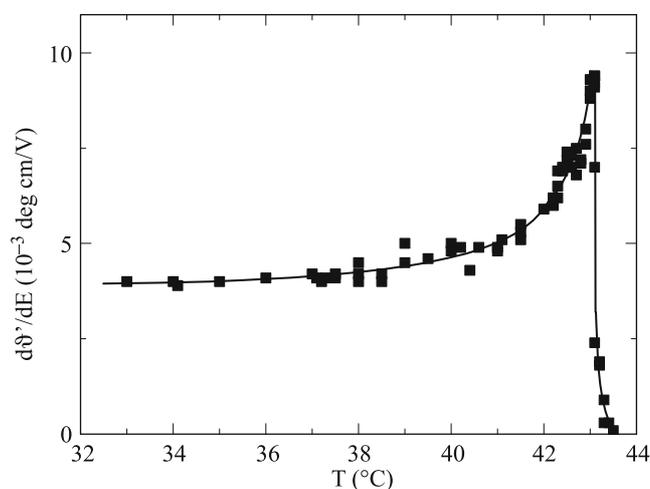

Fig. 4. Temperature dependence of apparent inclination angle of optic axis.
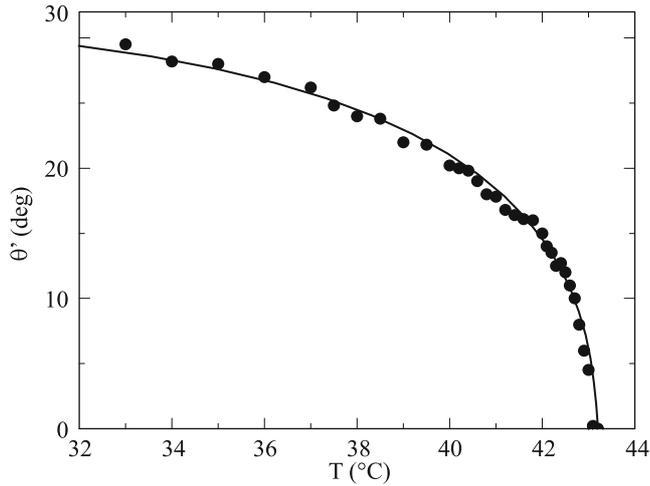
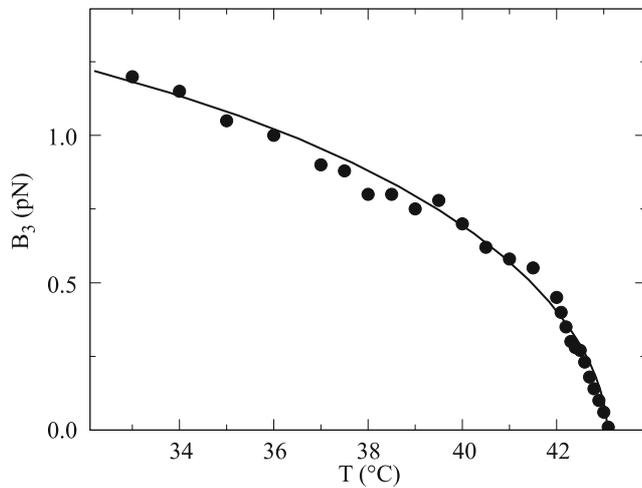Fig. 5. Temperature dependence of apparent tilt angle.

Fig. 6. Temperature dependence of twist elastic constant of **c**-director.

The elasticity coefficient B_3 obeys the potential law, $A \cdot (1 - T/T^*)^\alpha$, where T^* is the critical temperature equal to the SmA - SmC* transition temperature T_{CA} and α is the critical exponent. The temperature dependences of pitch, spontaneous polarization, tilt angle and optic axis inclination angle can be expressed in a similar way. The experimental values of the coefficients A and α for various physical quantities are collected in Table 1.

Table 1. Fitting parameters A and α for various physical quantities in the SmC*-phase of C8.

Quantity	A	Units	α
θ	78.4	deg	0.29
P_S	9.3	nC/cm^2	0.42
$\dfrac{d\vartheta'}{dU}$	11.7×10^{-3}	deg/V	-0.20
p	0.944	μm	-0.26
B_3	5.1×10^{-12}	N	0.42

As it can be seen from Table 1, the critical exponents for the tilt angle θ and the spontaneous polarization P_S differ from each other. This indicates that the spontaneous polarization is not proportional to the tilt angle. This observation can be understood assuming that the rotational freedom of the transversal component of the dipole moment of the molecule decreases with the decrease in temperature stronger than the tilt angle. A large contribution of the flexoelectric effect to the spontaneous polarization can be another source of this discrepancy [26]. The flexoelectric component of the spontaneous polarization is proportional to $q \cdot \theta$ and α for the pure flexoelectric effect amounts to 0.49 [26]. A combination of flexo- and piezo-effects could give a temperature dependence of the spontaneous polarization similar to critical one with a "critical" exponent $0.29 < \alpha < 0.49$. The measured value $\alpha = 0.42$ lies within this range.

Special attention should be paid to the determination of the helical pitch p to ensure proper values of the elastic constant B_3. The pitch should be measured with high accuracy because its square appears in Eq. (6). A stress present in the helix can influence the response of the optic axis of the sample to the electric field. The best way to avoid the influence of stress on the determined values of the elastic constant is measuring the pitch and the inclination of the optic axis ϑ at the same time or, at least, in the same sample geometry. Therefore, we used the results of the pitch measurements in homeotropic samples for calculation of B_3. The results of the pitch measurements in planar oriented samples can be strongly influenced by surface interactions giving an apparent decrease in pitch near the transition to the smectic A phase [24] and hence erroneous values of the elastic constant B_3.

The elastic constant B_3 vanishes at the phase transition SmC$^* \rightarrow$ SmA. It is not surprising, because this parameter describes the properties of the **c**-director vanishing at this transition. The critical exponent of B_3 is equal to the critical exponent of the spontaneous polarization.

The comparison of our experimental results with the literature data is difficult because the data on bulk material constants are very scarce. Up to now, the measurements of the bulk elastic coefficient B_3 in weak fields were reported only in Refs. 10 and 16. The values of B_3 obtained in these papers are similar to that presented here (0.5×10^{-12} N, 1×10^{-12} N and 0.9×10^{-12} N respectively, at temperature 3 K below T_{CA}). However, data obtained for planar samples scatter much more (see for instance Refs. 6, 27, 28, and 29). Most of them are based on dielectric measurements which are strongly dependent on the sample geometry [30,31]. However, any conclusive statements are difficult to formulate as the results concern different materials.

5. Conclusions

In this study, a method of determination of the elastic coefficient in smectic C* phase was presented. The method was based on the fact that ferroelectric liquid crystals are easily

deformed by an electric field. The calculation of the twist elastic constant B_3 for the smectic **c**-director requires the knowledge – besides known parameters like spontaneous polarization, pitch, tilt angle – of the inclination of the optic axis due to the electric field. The method fulfils the requirement of small deformation. Hence, it seems to be the proper one for determination of bulk values of the considered coefficient. We get reasonable results for the examined material C8. In contrast, the most frequently used planar alignment of samples could provide false results and might be applied only after checking that it gives some results as any method of small deformation.

Acknowledgements

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