Temperature dependence of the rotatory power in the SmC* phase of DOBAMBC

A. Seppen, I. Muševič, G. Maret, B. Žekš, P. Wyder, R. Blinc

J. Phys. France **49** (1988) 1569-1573 SEPTEMBRE **1988,** PAGE 1569

Classification
Physics Abstracts
61.30 — 64.70M — 78.20E

Temperature dependence of the rotatory power in the SmC* phase of DOBAMBC

A. Seppen, I. Muševič [1], G. Maret, B. Žekš [1], P. Wyder and R. Blinc [1]

Max-Planck-Institut für Festkörperforschung, 166 X, 38042 Grenoble, France
[1] Jozef Stefan Institute, E. Kardelj University of Ljubjana, Yugoslavia

(*Reçu le 29 mars 1988, accepté le 6 mai 1988*)

Résumé. — Des mesures précises de la variation en température du pouvoir rotatoire optique $\rho(T)$ sont présentées pour la phase SmC* du cristal liquide ferroélectrique DOBAMBC. L'approche de la transition SmC*-SmA est tout particulièrement examinée. Ces mesures associées à celles du pas de l'hélice permettent de déterminer l'angle d'inclinaison des molécules dans cette structure. Il s'agit, à notre connaissance, de la première mesure optique de cet angle dans une phase SmC* non perturbée, c'est-à-dire sans débobiner l'hélice. Nos mesures de l'inclinaison sont comparées avec celles obtenues dans la structure débobinées et brièvement discutées dans le cadre des modèles théoriques.

Abstract. — High resolution measurements of the temperature dependence of the optical rotatory power $\rho(T)$ in the SmC* phase of the ferroelectric liquid crystal DOBAMBC are presented. Special emphasis is on the region near the SmC*-SmA transition. These data together with measurements of the pitch allow for a determination of the molecular tilt angle in the helicoidal structure. This is believed to be the first optical measurement of the tilt in an unperturbed SmC* phase, i.e. without unwinding of the helix. The measurements of the tilt angle in this case are compared with those on the unwound structure and are briefly discussed in connection with theory.

Introduction.

In 1980 bistability and submicrosecond switching in thin ferroelectric SmC* samples was demonstrated [1] and moreover the feasibility for displays. In view of these potential applications of ferroelectric liquid crystals the behaviour of the tilt angle of the molecules with respect to the normal of the smectic layers and the spontaneous polarisation near the SmC*-SmA phase transition has become a subject of considerable interest during the last years [2]. There exist several different theoretical models [3-6] describing the temperature dependence of the molecular tilt, the spontaneous polarisation and the pitch in the helicoidal SmC* phase. In the context of these theories the question whether the molecular tilt and the spontaneous polarisation are strictly proportional to each other is of importance.

Optical measurements of the tilt angle have been performed in samples where the helicoidal structure is destroyed (unwound) by a strong electric field [7-13]. However, it cannot be excluded that orientation effects and the chemical instability of these liquid crystals under field may influence the tilt angle obtained by this method. Therefore so far it has not been possible to draw a firm conclusion about the relevance of the different theoretical models.

Here we show that the temperature dependence of the tilt angle in an *unperturbed* sample can be determined by the temperature dependences of the optical rotatory power and the pitch in such a sample.

Theory.

De Vries [14] discussed the optical rotation of linearly polarised light propagating along the helical axis in cholesteric liquid crystals. It was shown by Parodi [15] that the De Vries theory for cholesterics can be applied to chiral smectics C if effective refractive indices, as will be given in equations (2a) and (2b), are used. According to this theory [15] the rotatory power ρ of the SmC* phase for nearly circularly polarized propagation modes may be written as

$$\rho = -\frac{2\pi}{p}\frac{\alpha^2}{8\lambda'^2(1-\lambda'^2)} \quad (1)$$

where α is a function of the refractive indices : $\alpha = (\tilde{n}_e^2 - \tilde{n}_o^2)/(\tilde{n}_e^2 + \tilde{n}_o^2)$, λ' is the reduced wavelength $\lambda' = 2\lambda/p(\tilde{n}_e^2 - \tilde{n}_o^2)$, λ is the vacuum wavelength of light and $\tilde{n}_e$ and $\tilde{n}_o$ are the effective local indices of refraction [15] :

$$\tilde{n}_e^2 = \frac{n_1^2 n_3^2}{n_1^2 \sin^2 \theta + n_3^2 \cos^2 \theta} \tag{2a}$$

$$\tilde{n}_o^2 = n_2^2 . \tag{2b}$$

The reference frame is chosen such that both the wave vector of the helix $\mathbf{k}_c$ and of the light are in the z-direction, which makes a tilt angle θ with the molecular 3-axis of the dielectric susceptibility tensor ε. The 2-axis is normal to the tilt plane and the 1-axis perpendicular to both the 2- and 3-axis. In general smectics C are biaxial [16] and so refractive indices in these 3 independent directions in particular the 1- and 2-directions may display quite different behaviour.

We are interested in the temperature region near the SmC*-SmA phase transition where the tilt angle θ is small and the biaxiality is low, $n_1 \simeq n_2$. In this approximation equation (1) can be written as

$$\rho = -\frac{\pi p}{8} \frac{(n_3^2 - n_1^2)^2 \dfrac{n_1^4}{n_3^4} \sin^4 \theta}{(n_1^2 + n_2^2)^2} \times \frac{1}{\lambda^2 \left(1 - \dfrac{2\lambda^2}{p^2(n_1^2 + n_2^2)}\right)} . \tag{3}$$

Rearranging equation (3) gives for the tilt angle :

$$\theta = \arcsin \left(-\rho \frac{8}{\pi p} \frac{(n_1^2 + n_2^2)^2}{(n_3^2 - n_1^2)^2 \dfrac{n_1^4}{n_3^4}} \times \lambda^2 \left(1 - \frac{2\lambda^2}{p^2(n_1^2 + n_2^2)}\right)\right)^{1/4} . \tag{4}$$

The temperature dependence of the tilt angle is largely determined by the temperature dependences of the rotatory power and the helical pitch, which we have both measured. The contribution of the temperature dependences of the refractive indices is small [17, 18], yet will be incorporated [18].

As the pitch is finite at the SmC*-SmA transition while the tilt angle goes to zero, one can except that the rotatory power will continuously go to zero on approaching T_c. Also, the rotatory power should reflect the pronounced temperature dependence of the pitch.

In order to check the validity of the *De Vries* expression (4) for the rotatory power in the SmC* structure, the dispersion of the rotatory power $\rho(\lambda)$ is measured. For the ratio of $\rho(\lambda_1)$ and $\rho(\lambda_2)$ measured at two different wavelengths λ_1 and λ_2 we obtain by simply rewriting equation (1) for the two wavelengths :

$$\frac{\rho(\lambda_1)}{\rho(\lambda_2)} = C(\lambda_1, \lambda_2) \frac{\lambda_2^2}{\lambda_1^2} \frac{1 - \lambda_2'^2}{1 - \lambda_1'^2} \tag{5}$$

where $C(\lambda_1, \lambda_2)$ is nearly temperature independent, the main contribution coming from the weak temperature dependence of the refractive indices.

Experimental.

The set-up for the rotatory power measurements is analogue to that of Maret and Weill [19] for measuring birefringence. In the case of rotatory power measurements the rotation of light polarization after passing the sample is compensated by a Faraday rotator [20]. A modulation of the direction of the light polarisation is made by a photo-elastic modulator [21] in combination with a $\lambda/4$ plate. The angular resolution was about 5×10^{-4} rad. A two stage temperature controlling system stabilized the sample within 5 mK. More experimental details can be found in reference [22].

Sample cells were made of two glassplates, which, after cleaning, were coated with lecithin in order to obtain a homeotropic alignment in the SmA phase, and spaced with 2 strips of 75 μm thick Mylar foil. The cells were filled with DOBAMBC [23, 24] (p-decyloxybenzylidene p'-amino 2-methylbutylcinnamate) by capillary sucking of the material in the isotropic phase. Slowly cooling down into the SmC* phase resulted in a homogeneous sample with the helical axis perpendicular to the glass surfaces. The geometry of the sample in the experiment is given in figure 1. SmA-SmC* transition temperatures were in the range of 93 °C-92 °C.

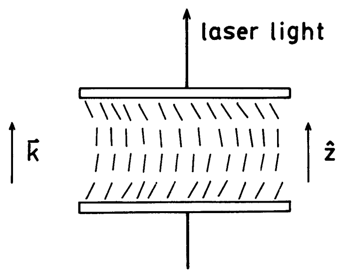

Fig. 1. — The geometry of the sample in the rotatory power experiment. The wave vector of the helical structure is perpendicular to the wall surfaces.

The measured rotatory power.

In this experiment one is only interested in the optical activity due to the long range helical structure present in the SmC* phase. Besides this there is the natural background optical activity caused by the chirality of the molecules (present even in the absence of long range order). The results for the optical activity of this phase will therefore be given relative to that at the SmA-SmC* phase transition temperature T_c.

The measured temperature dependence of the rotatory power ρ in the SmC* phase is presented in figure 2 for three different incident laser light wavelengths. Curve a is for $\lambda_1 = 488$ nm ; curve b for $\lambda_2 = 515$ nm. Curve c consists of two sets of data points both with $\lambda_3 = 647$ nm. During the experiment it was possible to switch only between two wavelengths ; curve a and a part of curve c were measured nearly simultaneously, and the same holds for curve b and the other part of curve c. The good agreement between the two different groups of measurements of curve c indicates the good reproducibility of these results.

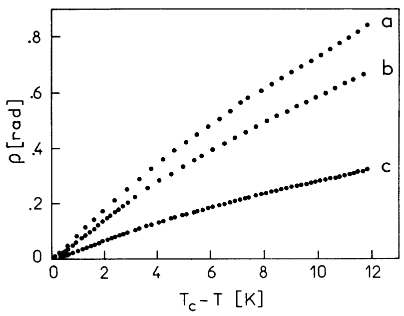

Fig. 2. — The measured rotatory power as a function of temperature for three different wavelengths ; (a) for $\lambda_1 = 488$ nm ; (b) for $\lambda_2 = 515$ nm and (c) for $\lambda_3 = 647$ nm.

The optical activity of DOBAMBC in the SmC* phase has already been measured with $\lambda = 632.8$ nm by Pieranski *et al.* [2] and Takezoe *et al.* [25]. The results given in curve c of figure 2 are in agreement with the results of these authors.

We found that the ratios $\rho(\lambda_1)/\rho(\lambda_3)$ and $\rho(\lambda_2)/\rho(\lambda_3)$ are temperature independent within the experimental accuracy and that the values for these ratios agree within 3 % with equation (5). We therefore conclude that the *De Vries* theory for the rotatory power can be applied to the SmC* phase of DOBAMBC.

The most interesting temperature region is that close to the SmC*-SmA transition temperature T_c. High resolution ρ measurements were performed in the interval T_c - 1.2 K up to T_c (Fig. 3). The results show that $\rho \to 0$ as $T \to T_c$ from below and reveal a weak bump in the interval T_c - 0.7 K to T_c - 0.4 K. As outlined below we attribute this to the known anomaly in the temperature dependence of the pitch in this region.

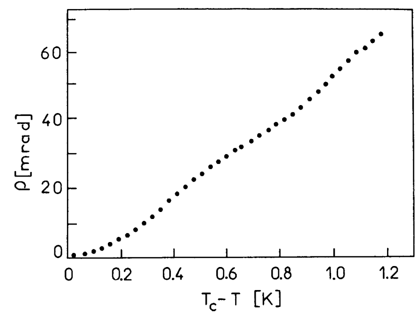

Fig. 3. — The rotatory power behaviour near T_c ($\lambda = 515$ nm).

The obtained tilt angle behaviour.

In order to determine the temperature dependence of the tilt angle of the molecules, $\theta(T)$ one needs to know in addition $p(T)$ and the refractive indices at the wavelength used according to equation (4). The measurements of $p(T)$ were taken in the geometry with the helical axis parallel to the cell walls and the smectic layers perpendicular to these boundaries. In this case that the molecules are aligned (nearly) parallel to the walls they are more hindered in changing their azimuthal angle than in the case where the molecules are (nearly) perpendicular to the walls. Therefore the measurements of $p(T)$ were performed on relativelly thick samples, e.g. of 245 μm thickness. Homogeneously aligned samples were slowly grown in a 10 tesla magnetic field. The pitch of the SmC* phase, as measured with laser diffraction ($\lambda = 647$ nm), is shown in figure 4. The althus obtained temperature dependence of the pitch is consistent with data [26] from selective reflection of homeotropic samples up to the last datapoint (at $T = T_c$ - 0.5 K) that can be measured by the reflection method. The anomaly in the temperature dependence of the pitch appears at about 0.5 K below T_c. Close to the transition temperature the pitch has a constant value of about 1 μm. In the rotatory power the observed bump appears to be in the same temperature range as that for the pitch anomaly.

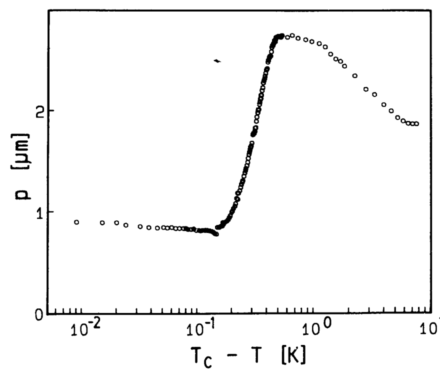

Fig. 4. — The temperature dependence of the periodicity of the helical structure in the SmC* phase.

Measurements of the refractive indices have been performed by Garoff [18]. We corrected them for the wavelength as deduced from reference [27] and extrapolated the values to T_c. The values obtained in this way are $n_1 = n_2 = 1.4783$ and $n_3 = 1.6969$ at $\lambda = 515$ nm. The temperature dependence of the tilt angle, calculated using equation (4), is given in figure 5. $\theta(T)$ is obtained by the measurement of $\rho(T)$ and $p(t)$, both performed on thick samples. This means that the inaccuracy in $\theta(T)$ caused by a possible bending of the smectic layers near the walls (chevron structured smectic layers [28]) is negligible.

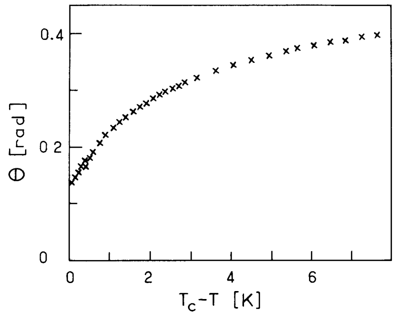

Fig. 5. — The temperature dependence of the tilt angle of the molecules in the SmC* phase.

Figure 6 shows the comparison of our results of $\theta(T)$ for the unperturbed SmC* phase of DOBAMBC with those obtained by unwinding the helix. Our results differ from those reported by Martinot-Lagarde *et al.* [10], but agree with those of Ostrovskii *et al.* [8] and Dumrongrattana *et al.* [13].

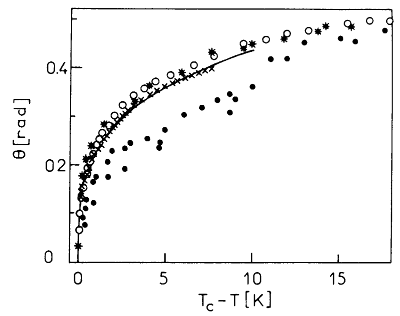

Fig. 6. — Measurements of $\theta(T)$ obtained by unwinding of the helix ; (•) data from reference [10], (*) data from reference [8] and (O) data from reference [13]. Our results obtained in an unperturbed helix structure : (x). The solid line is a fit to our results of the form $(T_c - T)^{\beta}$.

The solid line is a least squares fit to a function of the form $\theta = \theta_0\ (T_c - T)^{\beta}$. The best fitting parameters are $\theta_0 = 0.23$ and $\beta = 0.28$. One can see that this function roughly describes the behaviour over the whole temperature range investigated. However, at lower temperatures the exponent appears to be somewhat smaller than closer to T_c. In order to look more precisely at this feature, the $\rho(T)$ measurements close to T_c (Fig. 3) were also used to calculate $\theta(T)$. The T_c value found in $\rho(T)$ measurements is about 100 mK lower than T_c deduced from $p(T)$ measurement because of a slightly worse resolution of the ρ measurements. For the calculation of $\theta(T)$ the $\rho(T)$ data were shifted by 100 mK with respect to the $p(T)$ data. The behaviour of the tilt angle near T_c is presented in figure 7 on a double logarithmic scale. Again, close to T_c the exponent appears larger than further away. Consequently $\theta(T)$ cannot be described by a function of the simple form $(T_c - T)^{\beta}$.

Ordinary mean-field theory and a theory by Pikin and Indenbom [3] predict that the tilt angle should vary as $\theta(T) = \theta_0(T_c - T)^{\beta}$ with $\beta = 0.5$ and $\beta = 0.33$ respectively as compared to $\beta = 0.28$ from the data in figure 6. A generalised mean-field model for the SmC*-SmA phase transition proposed by Dumrongrattana and Huang [11], which is similar to the one suggested by Žekš [5], predicts a cross-over behaviour of $\theta(T)$; for $T_c - T \leq 1$ K (Ref. [12]) the exponent β is mean-field like ($\beta = 0.5$), whereas $\beta = 0.25$ at lower temperatures. Our measurements presented in figures 6 and 7 might eventually indicate the existence of two regimes, but we cannot exclude some influence due to the mismatch of pitch and rotatory power measurements.

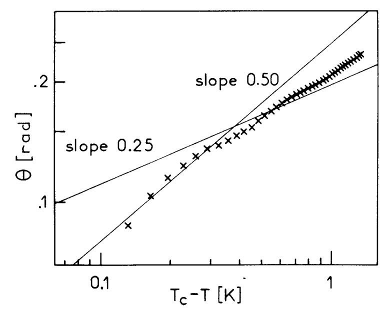

Fig. 7. — The temperature dependence of the tilt angle θ near T_c.

Conclusion.

For the ferroelectric liquid crystal DOBAMBC we have determined the tilt angle $\theta(T)$ from combined measurements of optical rotatory power and pitch near the SmC*-SmA transition. In this way we have obtained the temperature dependence of $\theta(T)$ of an unperturbed SmC* helicoidal structure. Our results essentially agree with the previous results on unwound samples. This agreement removes one of the main obstacles for testing theoretical models of the SmC*-SmA phase transition ; i.e. any disagreement between measured and predicted tilt angle $\theta(T)$ cannot be ascribed to the influence of helix unwinding. Our results are in favour of a generalized mean-field theory suggested by Dumrongrattana and Huang [11], and of a rather similar theory proposed by Žekš [5].

Acknowledgements.

We would like to thank H. Dresler for his technical assistance. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Dutch Organisation for the Advancement of Pure Research).

References

[1] CLARK, N. A. and LAGERWALL, S. T., *Appl. Phys. Lett.* **36** (1980) 899.

[2] PIERANSKI, P., GUYON, E., KELLER, P., LIÉBERT, L., KUCZYNSKI, W., PIERANSKI, P., *Mol. Cryst. Liq. Cryst.* **38** (1977) 275.

[3] PIKIN, S. A. and INDENBOM, V. L., *Sov. Phys. Usp.* **21** (1978) 487.

[4] OSIPOV, M. A. and PIKIN, S. A., *Sov. Phys. JETP* **55** (1982) 458.

[5] ŽEKŠ, B., *Mol. Cryst. Liq. Cryst.* **114** (1984) 259.

[6] HUANG, C. C. and DUMRONGRATTANA, S., *Phys. Rev. A* **34** (1986) 5020.

[7] MARTINOT-LAGARDE, Ph., *J. Phys. Colloq. France* (1976) C3-129.

[8] OSTROVSKII, B. I., RABINOVICH, A. Z., SONIN, A. S., STRUKOV, B. A. and CHERNOVA, N. I., *Sov. Phys. JETP Lett.* **25** (1977) 70.

[9] OSTROVSKII, B. I., RABINOVICH, A. Z., SONIN, A. S., STRUKOV, B. A. and TARASKIN, S. A., *Ferroelectrics* **20** (1978) 189.

[10] MARTINOT-LAGARDE, Ph., DUKE, R. and DURAND, G., *Mol. Cryst. Liq. Cryst.* **75** (1981) 249.

[11] DUMRONGRATTANA, S., HUANG, C. C., *Phys. Rev. Lett.* **56** (1986) 464.

[12] DUMRONGRATTANA, S., NOUNESIS, G. and HUANG, C. C. *Phys. Rev. A* **33** (1986) 2181.

[13] DUMRONGRATTANA, S., HUANG, C. C., NOUNESIS, G., LIEN, S. C. and VINER, J. M., *Phys. Rev. A* **34** (1986) 5010.

[14] DE VRIES, Hl., *Acta Crystallogr.* **4** (1951) 219.

[15] PARODI, O., *J. Phys. France* **36** (1975) Cl-325.

[16] TAYLOR, T. R., FERGASON, J. L. and ARORA, S. L., *Phys. Rev. Lett.* **24** (1970) 359.

[17] Note : The data for DOBAMBC in reference [18] cannot be described by the expressions of $n_1(T)$, $n_2(T)$ and $n_3(T)$ for AMC-11 given by GALERNE, Y., *J. Phys. France* **39** (1978) 1311.

[18] GAROFF, S., Thesis, Harvard University (1977) unpublished.

[19] MARET, G. and WEILL, G., *Biopolymers* **22** (1983) 2727.

[20] SPINDLER and HOYER Faraday modulator 04 0118.

[21] KEMP, J. C., *J. Opt. Soc. Am.* **59** (1969) 950.

[22] SEPPEN, A., Thesis, University of Nijmegen (1987) unpublished.

[23] MEYER, R. B., LIÉBERT, L., STRZELECKI, L. and KELLER, P., *J. Phys. Lett. France* **36** (1975) L-69.

[24] KELLER, P., LIÉBERT, L. and STRZELECKI, L., *J. Phys. France* **37** (1976) C3-27.

[25] TAKEZOE, H., FURUHATA, K., NAKAGIRI, T., FUKUDA, A. and KUZE, E., *Jpn. J. Appl. Phys.* **17** (1978) 1219.

[26] TAKEZOE, H., KONDO, K., MIYASATO, K., ABE, S., TSUCHIYA, T., FUKADA, A. and KUZE, E., *Ferroelectrics* **58** (1984) 55.

[27] KELKER, H. and HATZ, R., Handbook of liquid Crystals (Weinheim, Deerfield, Verlag Chemie) 1980, p. 257.

[28] RIEKER, T. P., CLARK, N. A., SMITH, G. S., PARMAR, D. S., SIROTA, E. B. and SAFINYA, C. R., *Phys. Rev. Lett.* **59** (1987) 2658.