phys. stat. sol. (b) 119, 727 (1983)

Subject classification: 14.4.1; 2; 22.9

*J. Stefan Institute, E. Kardelj University of Ljubljana*1) *(a)*
*and Physics Laboratory, University of Nijmegen*2) *(b)*

Dielectric Study of the Modulated Smectic C*–Uniform Smectic C Transition in a Magnetic Field

By

I. Muševič (a), B. Žekš (a), R. Blinc (a), Th. Rasing (b), and P. Wyder (b)

The in-plane component of the dielectric constant of chiral smectic p-decyloxybenzilidene-p′-amino-2-methylbutyl cinnamate is measured as a function of temperature and magnetic field applied parallel to the smectic layers. The transition from the modulated smectic C* to the uniform smectic C phase is accompanied by a drop in the dielectric constant in analogy to the incommensurate–commensurate transition in ferroelectrics. The C*–C transition line exhibits a large hysteresis and the critical field for the unwinding of the helix increases with decreasing temperature except close to the λ-line. The obtained results are in qualitative disagreement with the predictions of the Landau-de Gennes model and seem to suggest a different mechanism for the unwinding of the smectic C* helix.

Die in der Ebene liegende Komponente der Dielektrizitätskonstante von chiralem smektischem p-Dezyloxybenziliden-p′-amino-2-methylbutyl-Cinnamat wird in Abhängigkeit von Temperatur und Magnetfeld gemessen, das parallel zur smektischen Schicht angelegt wird. Der Übergang von der modulierten smektischen C*- zur homogenen smektischen C-Phase wird von einem Knick im Verlauf der Dielektrizitätskonstante begleitet, ähnlich wie beim Übergang inkommensurabel–kommensurabel in Ferroelektrika. Die C*–C-Übergangskurve zeigt eine große Hysterese und das kritische Feld für Abwicklung der Helix steigt mit abnehmender Temperatur außer in der Nähe der λ-Linie. Die erhaltenen Ergebnisse befinden sich qualitativ im Gegensatz zu den Vorhersagen des Landau-de Gennes-Modells und scheinen auf einen unterschiedlichen Mechanismus für das Abwickeln der smektischen C*-Helix hinzuweisen.

1. Introduction

In chiral ferroelectric smectic C* liquid crystals [1] the tilt of the long molecular axis and the in-plane spontaneous polarization precess around the normals to the smectic layers as one goes from one smectic layer to another. The periodicity of the resulting helix will be, in the general case, incommensurate with the distance between the smectic layers. The helix disappears in strong enough electric [1, 2, 3, 4] (E) or magnetic [5, 6] (H) fields and the tilt and polarization directions become uniform in space. The unwinding transition between the modulated C* and the uniform smectic C phase is — to a certain extent — analogous to the incommensurate-commensurate (I–C) transition in crystalline ferroelectrics [7].

Here we present the results of a dielectric study of the unwinding of the helicoidal ferroelectric smectic C* liquid crystal p-decyloxybenzilidene-p′-amino-2-methylbutyl cinnamate (DOBAMBC) in an external magnetic field H applied parallel to the smectic layers.

---

1) P.O.B. 199, Jamova 39, 61001 Ljubljana, Yugoslavia.
2) 6525 Nijmegen, The Netherlands.

2. Theory

The Landau free energy density expansion describing the C*–C transition has in the present case the form [6, 8, 9]

$$g(z) = g_0 + \frac{1}{2} a(\xi_1^2 + \xi_2^2) + \frac{1}{4} b(\xi_1^2 + \xi_2^2)^2 + \Lambda\left(\xi_1 \frac{\partial \xi_2}{\partial z} - \xi_2 \frac{\partial \xi_1}{\partial z}\right) + $$
$$+ \frac{1}{2} K_{33}\left[\left(\frac{\partial \xi_1}{\partial z}\right)^2 + \left(\frac{\partial \xi_2}{\partial z}\right)^2\right] + \frac{1}{2\varepsilon}(P_x^2 + P_y^2) - \mu\left(P_x \frac{\partial \xi_1}{\partial z} + P_y \frac{\partial \xi_2}{\partial z}\right) +$$
$$+ C(P_x\xi_2 - P_y\xi_1) - \frac{1}{2}\chi_a H_x^2 n_x^2 - E_y P_y \,, \tag{1}$$

where

$$\xi_1 = n_z n_x \approx \theta \cos \Phi(z)\,, \qquad \xi_2 = n_z n_y \approx \theta \sin \Phi(z) \tag{2}$$

with θ being the tilt angle and $\Phi = \Phi(z)$ the azimuthal angle varying from layer to layer.

Here g_0 is the free energy density of the smectic A phase, n_x and n_y are the components of the molecular director $n = (n_x, n_y, n_z)$ with the z-direction being normal to the smectic layers, P_x and P_y are the components of the in-plane spontaneous polarization, $a = \alpha(T - T_0)$, $b > 0$, K_{33} is the elastic modulus, Λ the coefficient of the Lifshits term responsible for the modulated structure, μ and C the coefficients of the "flexo"- and "piezo"-electric-like coupling between the tilt and the polarization, and χ_a the diamagnetic anisotropy of the molecules. The external electric field which is applied perpendicular to the modulation direction and to H is assumed to be small so that the dielectric coupling [4], which is quadratic in the field, can be neglected. Similarly we assumed that the molecular tilt is small so that $n_z \approx 1$ and $\sin \theta \approx \theta$.

The free energy density (1) is analogous to the one [9, 10, 11] used to describe the paraelectric-incommensurate–commensurate transitions in crystals except for the fact that the anisotropy term driving the I–C transition is here of second order ($n = 2$), whereas [12] $n = 4$ in $(NH_4)_2BeF_4$, $n = 6$ in Rb_2ZnCl_4, etc. In the present case the anisotropy term, $1/2\chi_a H_x^2 n_x^2$, driving the C*–C transition is thus of the same order in n_x as the term $1/2\alpha(T - T_0)\,(n_x^2 + n_y^2)$ driving the transition from the smectic A to the smectic C* phase.

In the constant amplitude (CAA) approximation, $\theta = A = \text{const} \neq f(z)$, the minimization of $F = L^{-1}\int_0^L g(z)\,dz$ with respect to P_x, P_y, and Φ leads for $E = 0$ to the sine-Gordon equation [13] which admits non-linear phase soliton solutions for $H \neq 0$,

$$\frac{d^2\Phi}{dz^2} = \left(\frac{\chi_a H_x^2}{2\tilde{K}_{33}}\right) \sin (2\Phi)\,, \tag{3}$$

where $\tilde{K}_{33} = K_{33} - \varepsilon\mu^2$. Only for $H = 0$ the solutions are of the plane wave type [9] $\xi_1 = \theta \cos (qz)$, $\xi_2 = \theta \sin (qz)$, $q = \tilde{\Lambda}/\tilde{K}_{33}$, where $\tilde{\Lambda} = \Lambda - \varepsilon\mu C$. The critical field for the unwinding of the helix is here temperature independent [5, 13],

$$H_c = \frac{\pi}{4} \frac{2\tilde{\Lambda}}{(\tilde{K}_{33}\chi_a)^{1/2}}\,, \tag{4}$$

and the C*–C transition is of second order. In the presence of an external electric field applied perpendicularly to $\boldsymbol{H}$ and $\boldsymbol{q}$ the minimization of $F = L^{-1}\int_0^L g(z)\,dz$ leads in the CAA to the double sine-Gordon equation [10, 12, 14],

$$\frac{d^2\Phi}{dz^2} = C_1 \sin (2\Phi) + C_2 \sin \Phi\,, \tag{5}$$

where $C_1 = \chi_a H_x^2 / 2\tilde{K}_{33}$ and $C_2 = \varepsilon C E_y / A \tilde{K}_{33} \propto E_y$. The small field static dielectric susceptibility of the C* phase in the direction of the spontaneous polarization exhibits near the C*–C transition a Curie-Weiss law with a logarithmic correction,

$$\chi_{yy} = \left(\frac{\partial \langle P_y \rangle}{\partial E_y}\right)_{E_y \to 0} = \varepsilon + \frac{C_H}{(H_c - H_x)\left|\ln \dfrac{H_c - H_x}{H_c}\right|}\,; \qquad H_x < H_c\,, \tag{6a}$$

where $C_H = (C^2 \varepsilon / \chi_a H_c)$ is nearly field independent and small in the C phase,

$$\chi_{yy} \approx \varepsilon\,, \qquad H_x > H_c\,, \tag{6b}$$

χ_{xx} does not show any critical behaviour near the C*–C transition and is approximately equal to ε in both phases.

The above expressions are analogous to the temperature dependence of the dielectric constant near the I–C transition in incommensurate ferroelectric crystals [10]. The CAA represents, however, in the present case where $n = 2$, a much poorer approximation than at I–C transitions where $n \geqq 4$. Amplitude fluctuation effects [12] lead to a temperature dependence of H_c and may change the C*–C transition into a first-order one.

The Curie constant C_H for the magnetic field induced unwinding of the helix as given by (6a) should be compared with the Curie constant for the temperature induced incommensurate-commensurate transition in Rb_2ZnCl_4 and with the Curie constant C_T for the direct smectic A → smectic C transition for $H > H_c$. This latter transition is analogous to a normal paraelectric-ferroelectric transition with a Curie-Weiss type behaviour of the static susceptibility.

On approaching the smectic A → smectic C transition line from above for $H < H_c$ one finds

$$\chi_{yy} = \varepsilon + \frac{C_T}{T - T_c(H)}\,; \qquad T > T_c(H)\,, \qquad H > H_c\,, \tag{7a}$$

where

$$C_T = \frac{\varepsilon^2 C^2}{\alpha} \leqq \frac{P_0^2}{\vartheta_0^2 \alpha}\,. \tag{7b}$$

Here P_0 is the spontaneous polarization and ϑ_0 the spontaneous tilt. The equality sign in (7b) applies only to the case of a negligible flexoelectric coupling coefficient μ.

Since the spontaneous polarization in ferroelectric liquid crystals is much smaller than in solid ferroelectrics, one expects that C_T is much smaller than the Curie-Weiss constants usually found in crystalline ferroelectric phase transitions. A rough estimate using $P_0 = 3 \times 10^{-9}$ As/cm², $\vartheta_0 \approx 0.3$ rad, and $\alpha = 6 \times 10^3$ J/(m³K) yields $C_T \leqq 0.2$ K. This is indeed rather small if compared to the values $C_T = 10^4$ to 10^5 K found in solid ferroelectrics. Even at the incommensurate-commensurate transition in Rb_2ZnCl_4, $C_T \approx 80$ K.

It should be noted that the static dielectric susceptibility should not diverge on going from the Sm A to the Sm C* phase. The difference in the susceptibilities between the Sm A and Sm C* phases along the $H = 0$ line is given by

$$\chi_{C^*} - \chi_A = (\Delta\chi) = \frac{C^2 \varepsilon^2}{2\tilde{K}_{33} q^2} \leqq \frac{\varepsilon \alpha (T_c - T_0)}{2\tilde{K}_{33} q^2}\,; \qquad H = 0\,, \tag{8}$$

where $T_c - T_0$ is the difference in the transition temperatures between chiral DOBAMBC and a racemic mixture. For $T_c - T_0 \lessapprox 0.1$ to 0.08 K one finds with $C_T \leqq 0.2$ K that the dielectric susceptibility of the Sm C* phase exceeds that of the Sm A phase for $\Delta\chi \leqq 3$ to 5.

The Curie constant for the magnetic field induced unwinding of the helix is of the order of

$$C_{\mathrm{H}} \approx \frac{C_{\mathrm{T}}}{\Delta T} H_0 \geqq 100\ T\,, \tag{9}$$

where $\Delta T = T_c(H_0) - T_c(H = 0) \lessapprox 0.1$ K and $H_0 \approx 10$ T [13]. In contrast to the case of the Sm A → Sm C transition where C_{T} is small, the Curie constant C_{H} is so large that the predicted Curie-Weiss behaviour at the magnetic field induced unwinding of the helix should be easily observable. A measurement of the magnetic field dependence of the dielectric constant thus provides a rather stringent test of the mechanism of the unwinding of the helix.

3. Experimental Results and Discussion

The in-plane component of the dielectric constant of 75 μm thick monodomain samples has been measured at 20 Hz at an orientation where the ac electric field was perpendicular to the helicoidal axis and the direction of the external static magnetic field. The monodomain samples were prepared [13] by slowly (1 K/h) cooling the system through the isotropic–smectic A transition in a magnetic field of 10 T which was parallel to the sample walls. In this way all molecules oriented with their long axes parallel to the sample walls. After that the magnetic field was decreased to a very small value and the system was slowly cooled to the smectic C* phase. The sample was now rotated by 90° so that $\boldsymbol{q} \perp \boldsymbol{H} \perp \boldsymbol{E}$ (insert to Fig. 1).

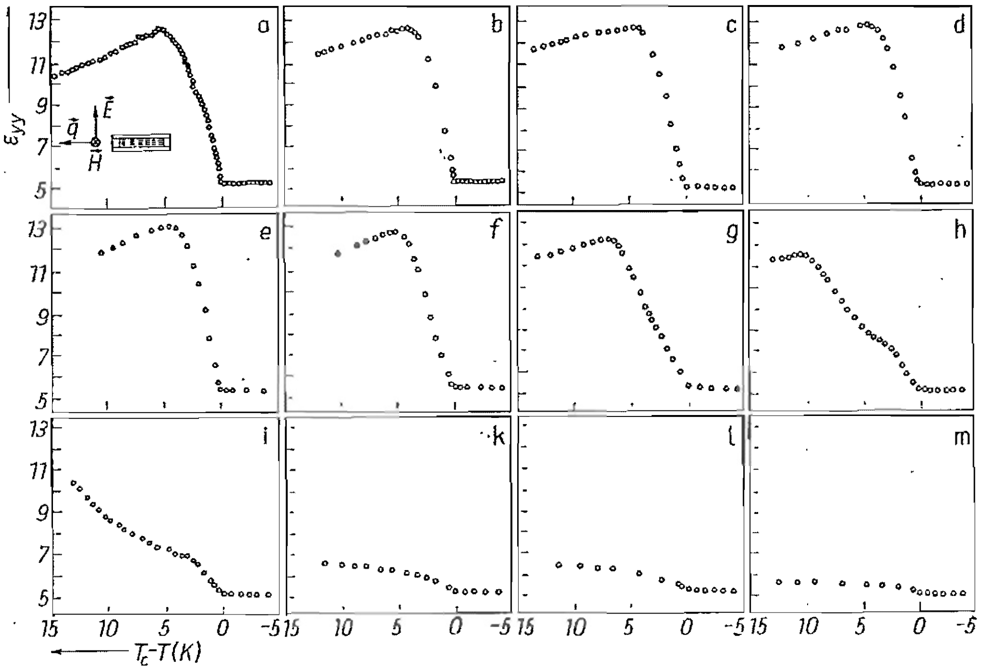

Fig. 1. Temperature dependence of the in-plane component ε_{yy} of the dielectric constant of DOBAMBC at different magnetic fields. The insert in a) schematically shows the sample geometry. a) $H = 0$, b) 1, c) 2, d) 3, e) 4, f) 5, g) 6, h) 7, i) 8, k) 11, l) 12, m) 13 T

The temperature dependence of the in-plane component ε_{yy} of the dielectric constant at $H = 0$, 1, 2, 3, 4, 5, 6, 7, 8, 11, 12, and 13 T is shown in Fig. 1. The data were obtained on slow cooling from the SmA phase and — away from T_c — qualitatively agree with the Landau theory. ε_{yy} is nearly temperature and magnetic field independent in the smectic A phase. From a value of about ≈ 5 in the smectic A phase ε_{yy} increases to about ≈ 12 in the smectic C* phase. At lower fields it increases sharply, reaches a peak, and then slowly decreases with decreasing temperature. At higher magnetic fields the anomaly around the smectic A -smectic C* transition becomes less pronounced and splits into two shoulders at fields above 7 T confirming the presence of a reentrant smectic C* phase [13]. The anomaly practically disappears at fields exceeding 11 T. No Curie-Weiss-like increase in ε_{yy} as predicted by (7a) could be observed at the A–C transition for $H > H_c$ within the resolution of this experiment. C_T is thus indeed rather small.

The magnetic field dependence of ε_{yy} around the smectic C*–C transition, as obtained from the data of Fig. 1, is shown in Fig. 2. ε_{yy} slowly increases with increasing magnetic field, reaches a peak (the position of which depends on temperature), and then drops to a rather low value in the smectic C phase. The value of ε_{yy} in the smectic C* phase is larger at larger T_c–T values, whereas the asymptotic value of ε_{yy} is temperature independent in the smectic C phase.

The magnetic field dependence of ε_{yy} away from H_c thus again qualitatively resembles the predicted behaviour [14]. The data close to H_c are, however, in qualitative

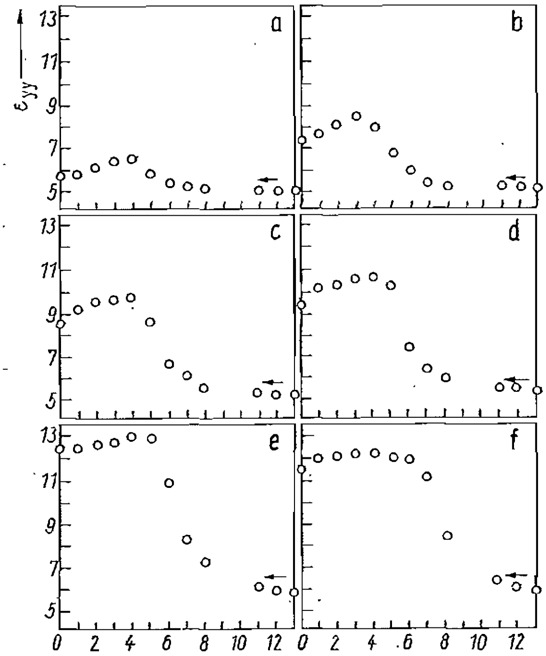

Fig. 2

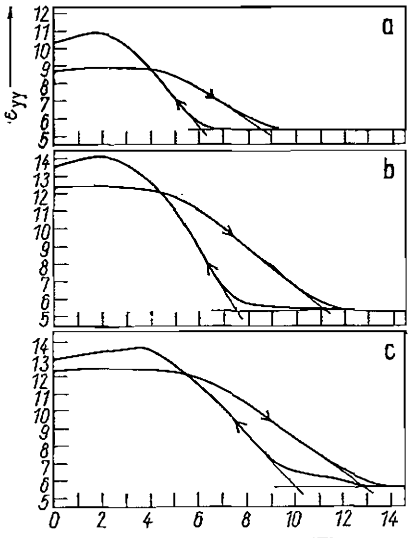

Fig. 3

Fig. 2. Magnetic field dependence of the dielectric constant ε_{yy} at different temperatures as evaluated from the data shown in Fig. 1: a) $T_c - T = 0.5$, b) 1, c) 1.5, d) 2, e) 5, f) 9K

Fig. 3. Fast passage magnetic field dependence of the dielectric constant of DOBAMBC at various temperatures: a) $T_c - T = 1.5$, b) 5, c) 11 K

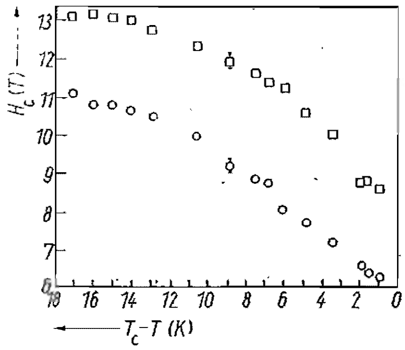

Fig. 4. Hysteresis of the C*–C transition line in DOBAMBC at temperatures well below the smectic A–smectic C* transition. ○ decreasing, □ increasing field

disagreement with the Landau-de Gennes model of the unwinding of the helix. No Curie-Weiss behaviour of the dielectric constant has been observed in spite of the large value of C_H predicted (9). The smearing out of the transition resulting in a finite value of ε_{yy} at $H = H_c$ and the gradual decrease of ε_{yy} with increasing field on going to the smectic C phase are in sharp contrast with the predictions of (6a, b). This discrepancy could be analogous to the difference between the predicted and observed temperature dependences of the dielectric constant in "dirty" incommensurate ferroelectrics [15]. In these systems "impurity" pinning of phase solitons plays an important role and results in metastable states where the phase soliton density differs from the equilibrium value.

To find out if the observed smearing out of the C*–C transition is indeed due to metastable states we decided to measure $\varepsilon_{yy} = \varepsilon_{yy}(H)$ at $T =$ const using relatively fast sweeps of the magnetic field. The whole sweep 0 to 14.5 T was performed in 10 min. The results are shown in Fig. 3 for $T_c - T = 1.5$, 5, and 11 K. The C*–C transition is still accompanied by a drop in the dielectric constant. The peak in ε has completely disappeared when one goes from the C* to the C phase. In the reverse direction there is, however, still a peak. This behaviour is again analogous to the temperature dependence of the dielectric constant at the I–C transition with impurity "pinning". The value of H_c depends on the direction of the change (Fig. 4) of the magnetic field. Except close to the λ-line H_c increases with decreasing temperature. The values of H_c derived from the temperature dependence of ε_{yy} at different magnetic fields agree with the H_c values for the C–C* transition at $T =$ const. This can be easily understood as, in view of the form of the C*–C transition line [1], at high magnetic fields one first enters on cooling the C and only later the C* phase. The hysteresis in the C*–C transition is huge (≈ 2 T) and the C*–C transition line is, in contrast to (4), not parallel to the T axis. This agrees with the optical data [13] on the C*–C transition which were obtained with a slowly increasing magnetic field.

4. Conclusions

The above data show that

(i) The unwinding of the smectic C* helix is indeed accompanied by a drop in the in-plane component of the dielectric constant.

(ii) The critical field for the unwinding of the helix depends on temperature in contradiction to the CAA predictions of the Landau-de Gennes model.

(iii) There is a huge hysteresis in the C*–C transition line in analogy to the I–C transition in incommensurate ferroelectrics.

(iv) The transition is smeared out and cannot be quantitatively described in terms of the Landau-de Gennes model for the unwinding of the cholesteric pitch.

(v) The question whether this is due to metastable states involving a phase soliton density which deviates from equilibrium or whether defects determine the unwinding process requires a further study.

References

[1] R. B. Meyer, L. Liebert, L. Strzelecki, and P. J. Keller, J. Physique, Lettres 36, L69 (1975).
[2] B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov, and N. I. Chernova, Zh. eksp. teor. Fiz., Pisma 25, 80 (1977).
[3] G. Durand and Ph. Martinot-Lagarde, Ferroelectrics 24, 89 (1980).
[4] R. Blinc and F. C. de Sa Barreto, phys. stat. sol. (b) 87, K105 (1978).
[5] P. G. de Gennes, Solid State Commun. 6, 163 (1968).
[6] A. Michelson, Phys. Rev. Letters 39, 464 (1977).
[7] Y. Ishibashi, Ferroelectrics 24, 119 (1980); R. A. Cowley, Adv. Phys. 29, 1 (1980).
[8] S. A. Pikin and V. L. Indenbom, Uspekhi fiz. Nauk 125, 251 (1978).
[9] R. Blinc and B. Žekš, Pys. Rev. A 18, 740 (1978).
[10] A. Levstik, P. Prelovšek, C. Filipič, and B. Žekš, Phys. Rev. B 25, 3419 (1982).
[11] D. G. Sannikov, J. Phys. Soc. Japan 49, Suppl. B, 75 (1980).
[12] P. Prelovšek, J. Phys. C 15, L269 (1982).
[13] I. Muševič, B. Žekš, R. Blinc, Th. Rasing, and P. Wyder, Phys. Rev. Letters 48, 192 (1982).
[14] O. Hudak, J. Physique 44, 57 (1983).
[15] K. Hamano, Y. Ikeda, T. Fuyimoto, K. Ema, and S. Hirotsu, J. Phys. Soc. Japan 49, 2278 (1980).

(Received June 13, 1983)