Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Dielectric and optical studies near the chiral smectic C-smectic A transition of (S)-2-hydroxy-4-decyloxybenzylidene-4'-amino-2p''-methylbutylcinnamate

A. Ezcurra[a]; M. A. Pérez Jubindo[a]; M. R. De La Fuente[a]; J. Etxebarria[b]; A. Remón[b]; M. J. Tello[b]
[a] Departamento de Fisica Aplicada II, Facultad de Ciencias, Universidad del Pais Vasco, Bilbao, Spain [b] Departamento de Fisica de la Materia Condensada, Facultad de Ciencias, Universidad del Pais Vasco, Bilbao, Spain

To cite this Article Ezcurra, A. , Jubindo, M. A. Pérez , De La Fuente, M. R. , Etxebarria, J. , Remón, A. and Tello, M. J.(1989) 'Dielectric and optical studies near the chiral smectic C-smectic A transition of (S)-2-hydroxy-4-decyloxybenzylidene-4'-amino-2p''-methylbutylcinnamate', Liquid Crystals, 4: 2, 125 — 132

To link to this Article: DOI: 10.1080/02678298908029066

URL: http://dx.doi.org/10.1080/02678298908029066

LIQUID CRYSTALS, 1989, VOL. 4, NO. 2, 125–132

Dielectric and optical studies near the chiral smectic C–smectic A transition of (S)-2-hydroxy-4-decyloxybenzylidene-4′-amino-2p''-methylbutylcinnamate

by A. EZCURRA, M. A. PÉREZ JUBINDO and M. R. DE LA FUENTE
Departamento de Fisica Aplicada II, Facultad de Ciencias,
Universidad del Pais Vasco, Apdo. 644, 48080 Bilbao, Spain

and J. ETXEBARRIA, A. REMÓN and M. J. TELLO
Departamento de Fisica de la Materia Condensada, Facultad de Ciencias,
Universidad del Pais Vasco, Apdo. 644, 48080 Bilbao, Spain

(*Received 6 July 1988; accepted 9 August 1988*)

The complex dielectric permittivity of HDOBAMBC has been measured in the vicinity of the chiral smectic C–smectic A transition as a function of temperature and frequency. The Goldstone mode contribution has been clearly identified and its relaxation frequency has been determined over the whole S_C^* range. High accuracy tilt angle measurements have also been performed by using a new method which allows its determination in a direct and virtually continuous way. These experimental results together with additional measurements of the polarization and helical pitch have been compared with those of DOBAMBC and analized in the framework of the generalized Landau theory. As for DOBAMBC a reentrant behaviour S_C^*–S_C–S_C^* has been observed under an electric field near the S_C^*–S_A transition.

1. Introduction

Ferroelectric liquid crystals were discovered in 1975 by Meyer *et al.* [1]. Since then, an increasing amount of experimental and theoretical work dealing with the thermodynamic properties of the chiral smectic C (S_C^*) phase has appeared. However, in spite of this intensive research activity, large differences exist among the experimental results of many important parameters characterizing the S_C^* phase [2–9] and the actual behaviour of some of them has only been recently clarified. From the theoretical point of view, the treatments which account for the temperature variations of the material parameters have been mainly restricted to the framework of the phenomenological theory of the S_C^*–S_A transition. It has been found that in order to obtain a proper description of all the experimental details, it is necessary to include at least eleven terms in the Landau free energy expansion [2, 9, 10]. However, most of these studies have been checked almost exclusively with the well-known ferroelectric (S)-4-decyloxybenzylidene-4′-amino-2p''-methylbutylcinnamate (DOBAMBC). Therefore it seems interesting to carry out an extensive characterization of other ferroelectric liquid crystals in order to contrast some of the unique features predicted for the S_C^*–S_A transition. Here we report measurements of the temperature dependence of the dielectric permittivity, spontaneous polarization, tilt angle, helical pitch and critical field of (S)-2-hydroxy-4-decyloxybenzylidene-4′-amino-2p''-methylbutylcinnamate (HDOBAMBC). The chemistry of this material has been described elsewhere [11, 12] as well as a preliminary characterization of its physical properties. The sequence of phase transition is

$$\text{crystal} \xrightarrow{88^\circ\text{C}} S_C^* \xrightarrow{109{\cdot}7^\circ\text{C}} S_A \xrightarrow{146{\cdot}8^\circ\text{C}} \text{isotropic}$$

We have compared our measurements with those corresponding to DOBAMBC and analysed our results in the framework of the so-called generalized Landau theory.

2. Experimental

Measurements of the dielectric permittivity and d.c. conductivity were carried out using the same experimental set-up as described in previous papers [13, 14]. The complex capacitance was determined in the 30Hz–1kHz frequency range with a Princeton Applied Research 5204 Lock-in Analyzer and the d.c. conductance with a picoameter HP4140B. The spontaneous polarization, P_s, was obtained by using the triangular wave method [15, 16]. The saturated current–voltage (I–V) cycles were recorded by a digital acquisition system HP7090A. The P_s values were obtained from the depolarization contribution of the helical reorientation to the total current. The frequency was set at 50 Hz and P_s was taken as the value for $V = 0$ in the integrated hysteresis loops. All of the equipment was interfaced to a microcomputer.

Cells for all of these measurements were made with gold-brass electrodes and an annular teflon ring 120 μm thick as the spacer. The measurements were performed on homogeneously aligned samples. Cells for optical measurements were made of two tin coated glass plates. Uniformly aligned samples were obtained by depositing a thin film of nylon 6/6 in the way described in [17] and rubbing only one of the plates so as to achieve maximum alignment [18]. The cell spacing was maintained by teflon spacers or simply by the use of glue at three cell edges without any spacers. Before the filling process, the cells were kept at 130°C for an hour in order to force the glue to de gas. The cells were filled by capillary action with the material in the isotropic phase. Samples were then cooled slowly (0·2°C/min) to the S_A phase and further down to the S_C^* phase.

The helical pitch of the S_C^* phase was determined by measuring the fringe distance in the stripe pattern shown by a thick sample ($\approx 100\,\mu$m) under the polarizing microscope. In order to overcome the influence of the wall anchoring effects and so obtain the free value of the helical pitch, we followed the procedure described in [19]. Critical field values were determined by measuring the voltages needed to suppress the dechiralization line pattern. It was found that the critical field clearly depends on the applied voltage variation rate, especially for low temperatures. The values reported here were obtained when a very slowly increasing field was applied to the sample.

To measure the tilt angle, θ, the sample was illuminated with circularly polarized light and subjected to a low-frequency bipolar square-wave voltage (0·1 Hz). The transmitted light was then analysed by a rotating analyser and detected by a photodiode. This signal was measured with a lock-in amplifier whose reference was fed from the rotating analyser. Under these conditions the relative phase between signals corresponding to the up and down states of the sample is just 4θ [20].

3. Results and discussion

Figure 1 shows the Cole–Cole plots for the low frequency complex dielectric permittivity at three different temperatures in the S_C^* phase. Measurements were

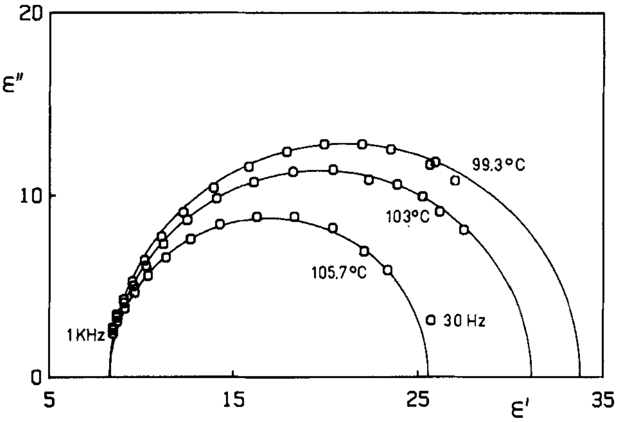

Figure 1. Cole–Cole plots for HDOBAMBC at three different temperatures in the chiral smectic C phase.

performed between 30 Hz and 1 kHz and the d.c. conductivity was subtracted from the measured losses. The experimental data can be fitted to a semicircle, which indicates that the relaxation process involved in this case follows the Debye law

$$\varepsilon(\omega) - \varepsilon_\infty = \chi_g/1 + i\omega\tau, \tag{1}$$

where χ_g is the static susceptibility associated with the so-called Goldstone mode, which is related to the helical structure. The Cole–Cole plots were obtained at twelve different temperatures in the S_C^* phase. The resulting relaxation frequency was found to be almost temperature independent, with a nearly constant value of 130 Hz.

Figure 2 shows the temperature dependence of the dielectric permittivity at 79 Hz. Two anomalies can be observed corresponding to the transition sequence: C–S_C^*–S_A. The S_C^*–S_A transition is characterized, as expected, by an additional contribution to ε', which has its origin in the helical structure. In the same figure we have represented by large dots the values of the static permittivity, $\varepsilon_s = \chi_g + \varepsilon_\infty$, obtained from the Cole–Cole diagrams. We can observe that ε' at 79 Hz is smaller than ε_s, indicating that at this frequency the Goldstone mode is already partially relaxed.

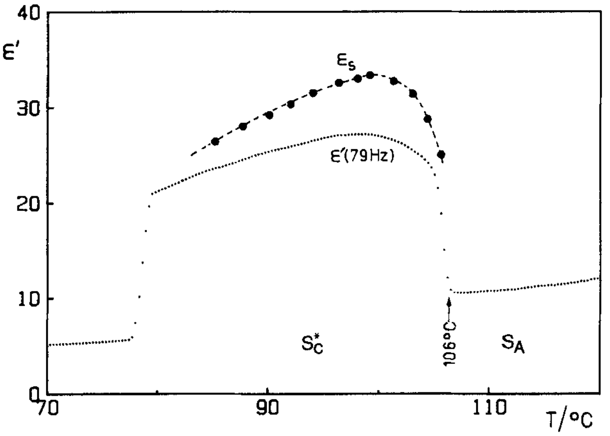

Figure 2. Dielectric permittivity at 79 Hz as a function of temperature (•): Static permittivity deduced from the Cole–Cole plots (●).

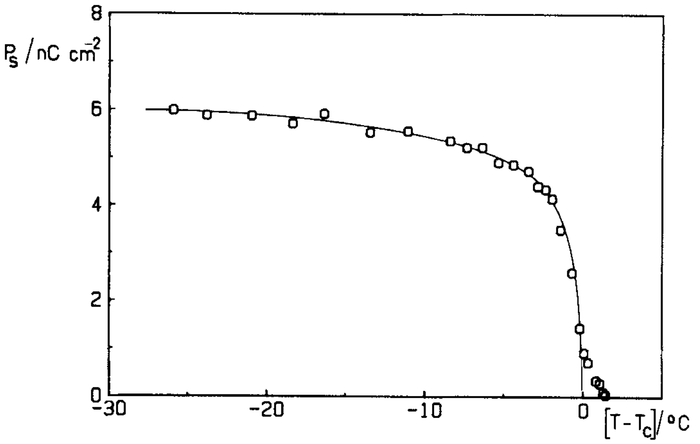

Figure 3. Temperature dependence of the polarization in the chiral smectic C phase. The tail above T_c is due to field induced effects.

Figure 3 shows the temperature dependence of the polarization values obtained with an electric field of 1·7 × 10^3 kV$_{pp}$/m. The dotted line serves as a guide to the eye and the tail for $T > T_c$, where T_c stands for the S_C^*–S_A transition temperature, is caused by field-induced effects. The spontaneous polarization of HDOBAMBC was also measured by Sakurai *et al.* [11]. As far as the temperature dependent behaviour is concerned, our results are similar to those [11], but their values are smaller than ours by about one third. The origin of such a great difference is not clearly understood though it may be due to several factors. For example, the sample conditions and test frequency were different in both cases. Another important aspect may be the measuring method. In our opinion our method is better to discriminate between the different contributions to the total current than the Sawyer–Tower method used by Sakurai *et al.* [11].

Figure 4 shows the temperature dependence of the tilt angle. The data were obtained both on heating and cooling at a temperature scanning rate of 1°C/min and

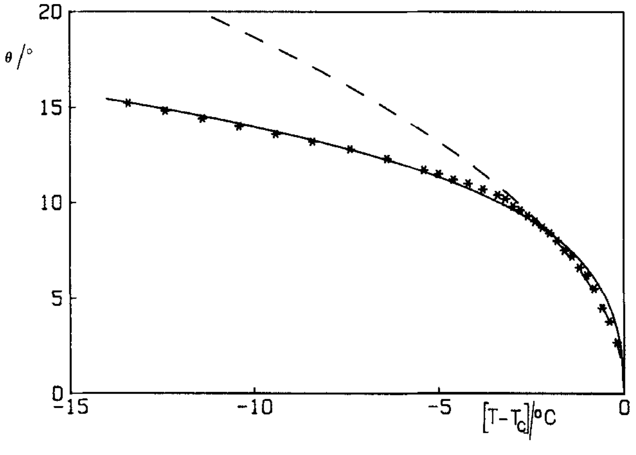

Figure 4. Temperature dependence of the tilt angle θ in the chiral smectic C phase (∗). The dashed line represents the fit to the mean field model and the solid line to the extended mean field model.

using a 12 μm sample and a square voltage of 0·1 Hz and ± 10 V. The original data exhibited a small finite-field effect at temperatures close to the phase transition, which produced a small tail in a temperature range of about 0·5°C. However, a plot of θ^2 versus T revealed a linear behaviour for about 3°C below the phase transition. This fact allowed us to make an accurate determination of the temperature at which the phase transition actually takes place and to eliminate the field-induced tilt contributions above the phase transition. The dashed line in figure 4 represents the least-squares fitting of our tilt angle data to the predictions of the mean-field model proposed in [21, 22]. Only the points down to 5°C below the transition were used in the fitting process because otherwise no reliable adjustment was possible. In contrast, the inclusion of only the three leading terms of the so-called extended mean-field model [23, 24] accounts much better for the data in the entire temperature range, as is clearly apparent from the good fit of the continuous line. Although the effect is here somewhat smaller than for the ferroelectric liquid crystal DOBAMBC, this last point confirms the importance of including a sixth-order term in the Landau free energy expansion in order to provide a quantitative explanation of the temperature behaviour of the tilt angle.

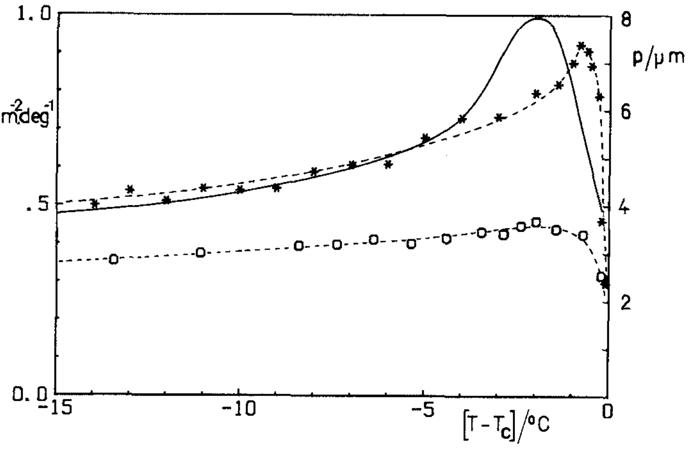

Figure 5. Temperature dependence of the helical pitch (*) and of the ratio P_s/θ (□) in the chiral smectic C phase. The solid line represents the best fit of the pitch to equation (2).

The necessity of adding new terms to the free energy expression of [21, 22] is more evident in the behaviour shown by the ratio P_s/θ. Although our measurements were performed on different samples, the anomalous dependence of P_s/θ predicted by the generalized Landau theory [2, 9, 25–28] is still clearly visible in our experimental results (see figure 5). Likewise, in a qualitatively similar fashion to that shown by DOBAMBC, the temperature dependence of the helical pitch appears to be closely connected with the dip of P_s/θ. Namely, the maximum of the pitch is attained in the temperature region where the knee of the P_s/θ curve occurs (see figure 5). This fact is in agreement with the theoretical models developed in [2, 9, 25–28].

Regarding the quantitative behaviour of the pitch, p, the theory predicts a linear relationship between the wavevector of the helical modulation q, P_s/θ and θ^2, i.e.

$$q = K^{-1}(\Lambda + fP_s/\theta + d\theta^2), \tag{2}$$

where K, Λ, f and d are coefficients of the Landau expansion: K is the elastic modulus, Λ the coefficient of the Lifshitz invariant term which accounts for the helical structure, f is the coefficient of the flexoelectric bilinear coupling and d is that corresponding to the $q\theta^4$ term of the free energy. The continuous line in figure 5 shows the best fit for our experimental data to equation (2). The calculated parameters are $K = 5{\cdot}1 \times 10^{-11}\,\mathrm{N}$, $\Lambda = 1{\cdot}96 \times 10^{-4}\,\mathrm{N\,m^{-1}}$, $f = -0{\cdot}61\,\mathrm{V}$ and $d = 1{\cdot}95 \times 10^{-4}\,\mathrm{N\,m^{-1}}$ (the value for K was previously estimated from our dielectric and critical field results as will be shown later). As can be seen, a good fit was not achieved and the theoretical curve only gives the qualitative tendency of the observed behaviour. This discrepancy seems to be fairly common among the compounds with a S_C^*–S_A transition, since it also occurs in a similar way for DOBAMBC [25, 26]. Therefore, more theoretical work to provide a quantitative explanation for this point appears to be necessary.

Concerning our dielectric measurements no attempt has been made to fit the experimental data to the predictions of the Landau theory. The final expressions are in this case very complicated and they involve too many parameters to allow us to find a unique and unambiguous fit. Instead we have tried to check the validity of an approximate expression reported in [9, 10, 28], which relates the Goldstone mode contribution to the static dielectric permittivity with the ratio $(P_s p/\theta)^2$. Since in our case there is no measurable contribution of the soft mode to the dielectric permittivity we must compare the values we obtained for χ_g and this expression

$$\chi_g = (8\pi^2 K)^{-1} (P_s p/\theta)^2. \tag{3}$$

Figure 6 shows the comparison between the dependence of χ_g and $(P_s p/\theta)^2$. As we can see, equation (3) does not hold in our case if the elastic modulus is to be independent of temperature. We believe that the main reason for this discrepancy is the same as for the bad fit to the pitch results. In fact the open circles in figure 6 have been obtained from the experimental curves, whereas equation (3) has been checked primarily for theoretical values of χ_g, p, P_s and θ. If our pitch results do not fit the theoretical predictions, any quantitity depending on them would not be reasonably expected to behave properly. Anyway, far from the transition, where all the anomalies and bad fits have disappeared the curves for both χ_g and $(P_s p/\theta)^2$ show a similar temperature dependence. In this temperature region the calculated value for the bulk modulus is $K = 5{\cdot}1 \times 10^{-11}$ N, which is somewhat higher than that of DOBAMBC.

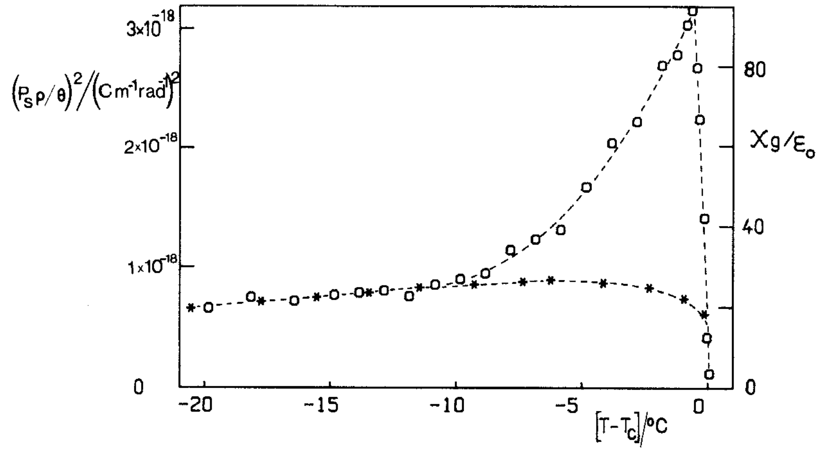

Figure 6. Comparison between χ_g (*) obtained from the Cole–Cole plots and the calculated ratio $(P_s p/\theta)^2$ (□).

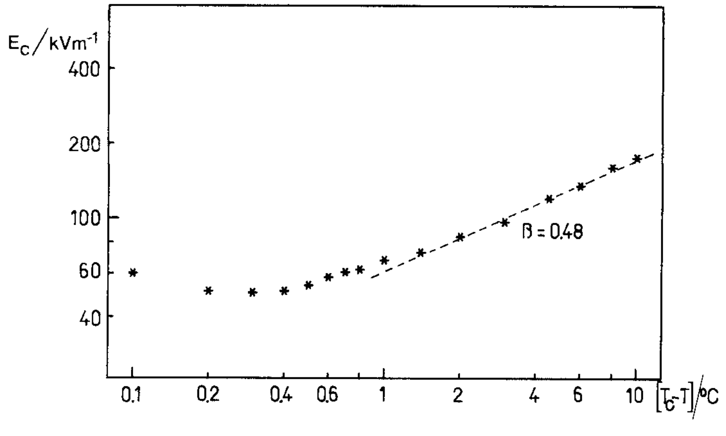

Figure 7. Log–log plot of the critical field versus temperature.

Nevertheless the associated elastic energy $(1/2)K\theta^2q^2$ resembles that of DOBAMBC and is, therefore, what is expected approximately for this compound.

As an extension of our characterization of the S_C^*–S_A transition of HDOBAMBC we shall discuss finally our critical field measurements. The temperature dependence of the critical field E_c is shown in figure 7 as a log–log plot of E_c versus $T_c - T$. The order of magnitude of the observed E_c values is well accounted by the formula

$$E_c = \pi^4 K\theta^2/(4P_s p^2), \qquad (4)$$

which can be obtained by comparing the elastic energy associated with the helix and the electrostatic energy associated with P_s and the applied field [1]. For example, using our experimental results for $T_c - T = 5°C$ we obtain $E_c = 50\,kV/m$ from equation (4), which is in reasonable agreement with the experimental result.

Regarding the shape of the E_c curve, a change of slope in the vicinity of the S_C^*–S_A phase transition can clearly be observed. In this region E_c increases with increasing temperature, which indicates the existence of a reentrant S_C^* phase. This reentrant behaviour in the phase diagram had already been observed for other ferroelectric liquid crystals in the presence of both electric [4, 29, 30] and magnetic [31] fields. Far from the S_C^*–S_A transition the E_c behaviour approximately follows the classical prediction [32] given by $E_c \sim (T_c - T)^{0.5}$, whereas near T_c the temperature dependence of E_c can be qualitatively explained by equation (4) and the anomalous behaviour of p near the S_C^*–S_A transition. However, a quantitative explanation of the phenomena around T_c seems still difficult to achieve. As pointed out in [4] the nucleation process of dechiralization pairs on the surfaces may play an important role and the same could be said about the tilt and azimuthal angle fluctuations near T_c [33]. The contributions of these processes should therefore be taken into account in order to achieve a complete description of all the observed features in the E_c behaviour.

References

[1] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P. J., 1975, *J. Phys., Paris*, **36**, L69.

[2] Dumrongrattana, S., and Huang, C. C., 1986, *Phys. Rev. Lett.*, **56**, 464.

[3] Martinot-Lagarde, Ph., 1976, *J. Phys., Paris*, **37-C3**, 129.

[4] Dumrongrattana, S., and Huang, C. C., 1986, *J. Phys., Paris*, **47**, 2177.

[5] Ostrovskii, B. I., Rabinovich, A. Z., Sonin, A. S., and Strukov, B. A., 1978, *Zh. eksp. teor. Fiz.*, **74**, 1748.

[6] Takezoe, H., Kondo, K., Miyasato, K., Abe, S., Tsuchiya, T., Fukuda, A., and Kuze, E., 1984, *Ferroelectrics*, **58**, 55.

[7] Parmar, D. S., Raina, K. K., and Shankar, J., 1983, *Molec. Crystals liq. Crystals*, **103**, 77.

[8] Benguigui, L. G., 1984, *Ferroelectrics*, **58**, 269.

[9] Levstik, A., Carlsson, T., Filipic, C., Levstik, I., and Zeks, B., 1987, *Phys. Rev.* A, **35**, 3527.

[10] Blinc, R., Filipic, C., Levstik, A., Zeks, B., and Carlsson, T., 1987, *Molec. Crystals liq. Crystals*, **151**, 1.

[11] Sakurai, T., Sakamoto, K., Honma, M., Yoshino, K., and Ozaki, M., 1984, *Ferroelectrics*, **59**, 21.

[12] Barberá, J., Meléndez, E., Serrano, J. L., and Sierra, M. T., 1988, *Ferroelectrics* (in the press).

[13] Pérez Jubindo, M. A., Ezcurra, A., Etxebarria, J., Remón, A., Tello, M. J., Marcos, M., and Serrano, J. L., 1988, *Molec. Crystals liq. Crystals*, **159**, 137.

[14] Pérez Jubindo, M. A., Ezcurra, A., de la Fuente, M. R., Santamaria, C., Etxebarria, J., Serrano, J. L., and Marcos, M., 1988, *Ferroelectrics* (in the press).

[15] Pérez Jubindo, M. A., Tello, M. J., and Fernández, J., 1981, *J. Phys.* D, **14**, 2305.

[16] Miyasato, K., Abe, S., Takezoe, H., Fukuda, A., and Kuze, E., 1983, *Jap. J. appl. Phys.*, **22**, L661.

[17] Patel, J. S., Leslie, T. M., and Goodby, J. W., 1984, *Ferroelectrics*, **59**, 137.

[18] Williams, D., and Davies, L. E., 1986, *J. Phys.* D, **19**, L37.

[19] Biradar, A. M., Bawa, S. S., Samanta, S. B., and Chandra, S., 1987, *Phys. Stat. Sol.* (*a*), **97**, 427.

[20] Etxebarria, J., Remón, A., Tello, M. J., Ezcurra, A., Pérez Jubindo, M. A., and Sierra, M. T., 1987, *Molec. Crystals liq. Crystals*, **150**, 257.

[21] Pikin, S. A., and Indembom, V. L., 1978, *Ferroelectrics*, **20**, 151.

[22] Blinc, R., and Zeks, B., 1978, *Phys. Rev.* A, **18**, 740.

[23] Dumrongrattana, S., Nounesis, G., and Huang, C. C., 1986, *Phys. Rev.* A, **33**, 2181.

[24] Nounesis, G., Huang, C. C., Pitchford, T., Hobbie, E., and Lagerwall, S. T., 1987, *Phys. Rev.* A, **35**, 1441.

[25] Huang, C. C., and Dumrongrattana, S., 1986, *Phys. Rev.* A, **34**, 5020.

[26] Huang, C. C., 1987, *Molec. Crystals liq. Crystals*, **144**, 1.

[27] Zeks, B., 1984, *Molec. Crystals liq. Crystals*, **114**, 259.

[28] Carlsson, T., Zeks, B., Levstik, A., Filipic, C., Levstic, I., and Blinc, R., 1987, *Phys. Rev.* A, **36**, 1484.

[29] Kondo, K., Takezoe, H., Fukuda, A., and Kuze, E., 1983, *Jap. J. appl. Phys.*, **22**, L43.

[30] Rozanski, S. A., and Kuczynski, W., 1984, *Chem. Phys. Lett.*, **105**, 104.

[31] Musevic, I., Zeks, B., Blinc, R., Rasing, Th., and Wides, P., 1982, *Phys. Rev. Lett.*, **48**, 192.

[32] Michelson, A., Benguigui, L., and Cabib, D., 1977, *Phys. Rev.* A, **16**, 394.

[33] Yamashita, M., and Kimura, H., 1982, *J. phys. Soc. Jap.*, **51**, 2419.