Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tlct20

Dielectric behaviour of the relaxational modes in a ferroelectric liquid crystal

J. Zubia [a c], A. Ezcurra [a], M. R. De La Fuente [a], M. A. Pérez Jubindo [a], T. Sierra [b] & J. L. Serrano [b]

[a] Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, 48080, Bilbao, Spain

[b] Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Zaragoza-CSIC, 50009, Zaragoza, Spain

[c] Departamento de Automática, Electónica y Telecommunicaciones, Escuela Técnica Superior de Ingenieros Industriales y de Telecomunicación, Universidad del País Vasco, Alameda de Urquijo s/n, 48013, Bilbao, Spain

Version of record first published: 24 Sep 2006.

LIQUID CRYSTALS, 1991, VOL. 10, NO. 6, 849–860

Dielectric behaviour of the relaxational modes in a ferroelectric liquid crystal

by J. ZUBIA†, A. EZCURRA, M. R. DE LA FUENTE* and M. A. PÉREZ JUBINDO

Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain

and T. SIERRA and J. L. SERRANO

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

(*Received 3 April 1991; accepted 22 June 1991*)

The dielectric response in 2-hydroxy-4-decyloxybenzilidene-4′-(2*S*-2-chloro-3-methylbutyloxy) aniline, a ferroelectric liquid crystal which shows a C–S_C^*–S_A–I phase transition sequence has been determined. The influence of a bias electric field, applied parallel to the smectic layers, on the parameters that characterize the contributions of the different modes to this response has been analysed. In addition to the soft mode and Goldstone mode contributions we have observed a low frequency relaxation mechanism which could be related to the defect structure present in samples with planar alignment. Moreover, the deconvolution process has allowed us to characterize the soft mode in the ferroelectric phase without unwinding the helical structure.

1. Introduction

In recent years considerable theoretical and experimental work has been devoted to the study of the dielectric response of ferroelectric liquid crystals with a S_C^*–S_A phase transition [1–6]. It is usually accepted that this response consists mainly of two relaxation modes, the soft mode and the Goldstone mode. The former is related to the amplitude changes of the director and the latter to the phase changes. Thus, it is interesting to obtain both contributions accurately and to determine their frequency and amplitude as a function of temperature. This point is specially difficult for the ferroelectric phase in which both contributions are present but with very different strengths, causing the soft mode to be drowned in the Goldstone mode. In order to discriminate one from the other, several strategies can be followed: to apply a DC field that destroys the helical structure causing the associated phenomena to disappear; to use a probing field with a frequency high enough to allow only the fast mechanism, etc. In addition, due to the quality and increasing accuracy of the dielectric measurements, new relaxational processes have appeared. Some of them have been explained as low

* Author for correspondence.

† Present address: Departamento de Automática, Electrónica y Telecommunicaciones, Escuela Técnica Superior de Ingenieros Industriales y de Telecomunicación, Universidad del País Vasco, Alameda de Urquijo s/n, 48013 Bilbao, Spain.

0267-8792/91 $3·00

frequency molecular relaxations [7] but in several cases no molecular explanation for the relaxations has been found [8–10].

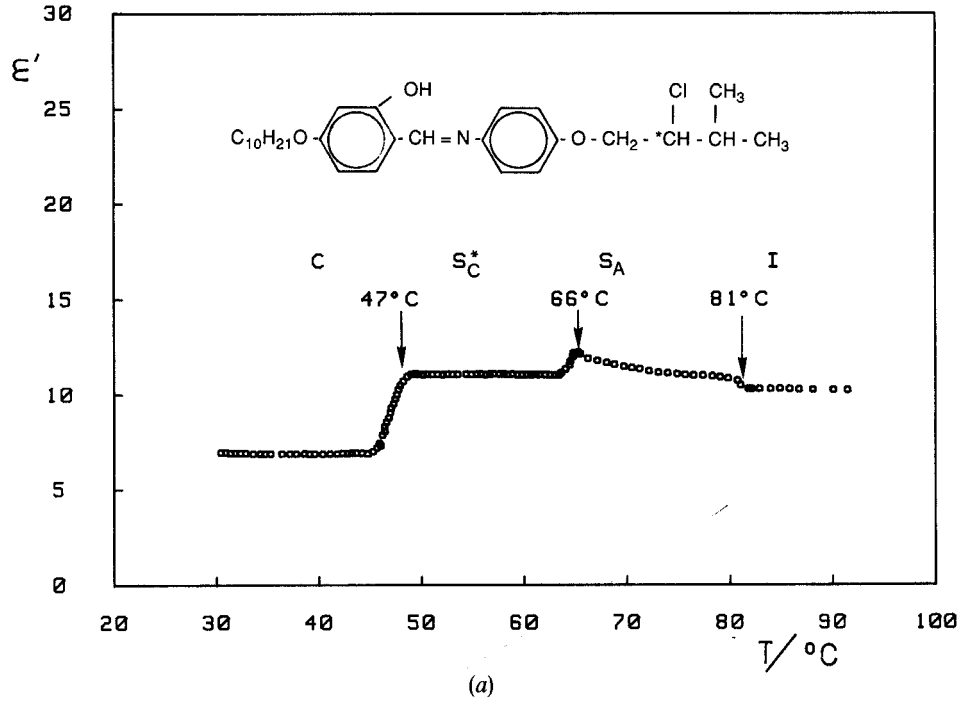
It is the aim of this paper to show and discuss the dielectric response of a ferroelectric liquid crystal around its S_C^*–S_A phase transition and to analyse the contribution of the different modes involved. In the paraelectric phase only one mode was obtained, whereas three modes are present in the ferroelectric phase. The study was performed with and without a bias field superimposed to the probing field. In the latter case, we shall show how the soft mode dielectric contribution could be obtained by deconvolution of the whole response without unwinding the helical structure by a bias field. Although the resolution is not very high, the interest of this kind of study is largely justified because the results are associated with a structure not disturbed by external fields. Another important point of this work is the study of the additional relaxation behaviour present in the ferroelectric phase, which is not usually observed. A possible relation between this contribution and the disorder in the planar structure of the material is discussed.

2. Experimental

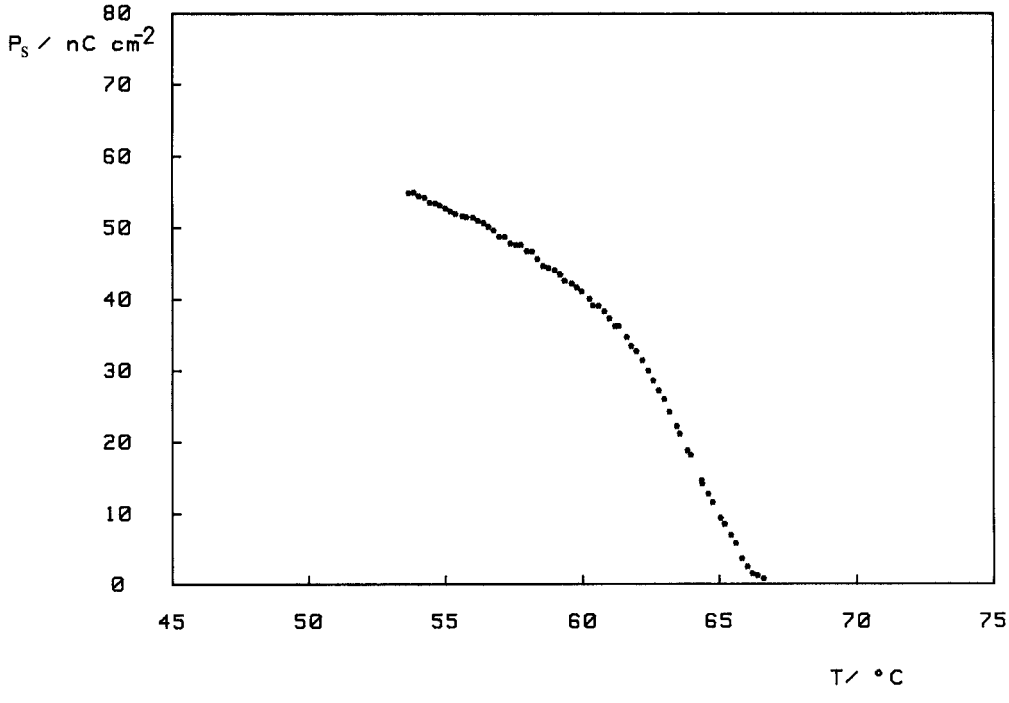
The liquid crystal used in this work was synthesized by Sierra *et al.* [11] and is 2-hydroxy-4-decyloxybenzilidene-4′-(2*S*-2-chloro-3-methylbutyloxy) aniline. The molecular structure of the compound together with its phase sequence and dielectric constant, ε', as a function of temperature are shown in figure 1 (*a*). The temperature dependence of the spontaneous polarization as obtained by using the triangular wave method [12] is shown in figure 1 (*b*). The helical pitch was found to be smaller than 1 μm over the whole S_C^* phase.

Dielectric measurements were carried out using the same experimental set-up described in [13]. The complex capacitance was measured in the frequency range 100 Hz–5 MHz using a HP4192A impedance analyser. A measuring voltage of 1 V_{pp} was applied in a direction parallel to the smectic layers. Different values for the bias voltage from zero to 35 V were applied in order to obtain different conditions for the helical structure in the S_C^* phase and to determine the dependence on the DC electric fields of the modes in both phases.

The temperature of the sample was controlled with a heating gas system and was stabilized to an accuracy of 0·01 °C. Two kinds of measuring cells were used; one of them consisted of two gold brass electrodes separated by a 80 μm thick annular teflon ring. This kind of cell allows us to eliminate the relaxation present when using low conductivity electrodes which is due to the RC circuit formed [14]. It does not allow optical control of the alignment but it is the most adequate for a relaxation study. In the other cell, which allows an optical check of the alignment state, the sample is held between two tin oxide coated glass plates (ITO) and planar alignment is achieved by depositing a thin film of nylon 6/6. The cell thickness was 85 μm. In both cases, the sample introduced was slowly cooled down from the isotropic phase to the S_A phase. When using the cell with metal electrodes, a magnetic field was applied in order to achieve a good alignment. As previous experiments have shown, an AC field yields planar alignment in materials with a S_C^*–S_A phase transition sequence, but different planar domains, with different directions for the helical axis can appear. As we shall explain later, this situation was tested optically with ITO cells in which similar conditions to those described were reproduced, and the expected structure was obtained.



(*a*)



(*b*)

Figure 1. (*a*) Molecular structure, phase sequence and temperature dependence of the dielectric permittivity at a frequency of 105 kHz of the compound studied. (*b*) Spontaneous polarization versus temperature.

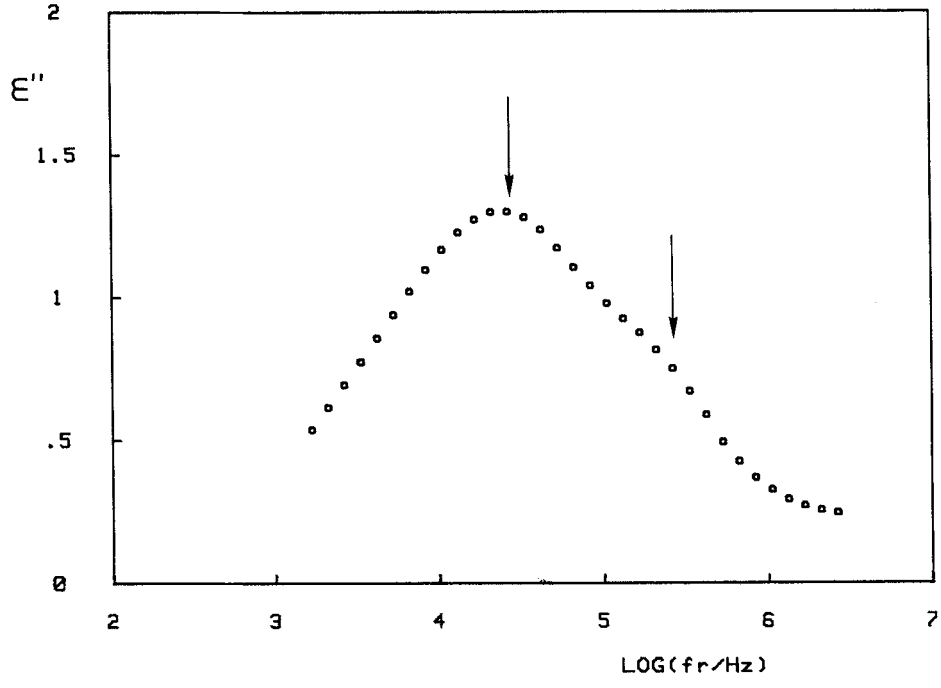
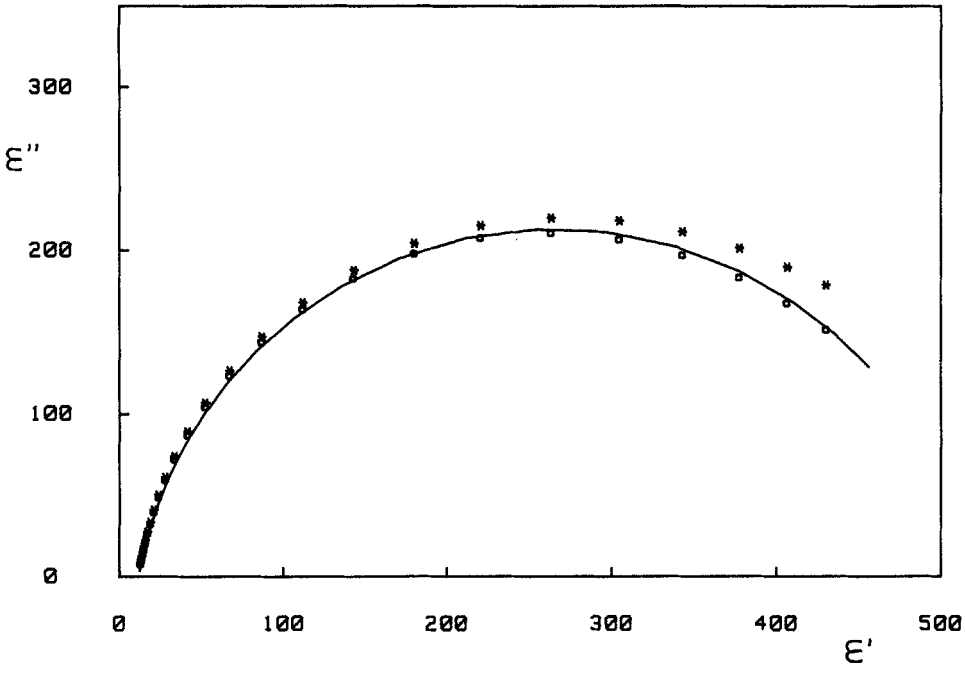


Figure 2. Dielectric losses in the S_C^* phase under a biasing field of 4·37 kV cm^{-1}. Two different relaxations, whose well separated relaxation frequencies are shown by arrows, can be distinguished.

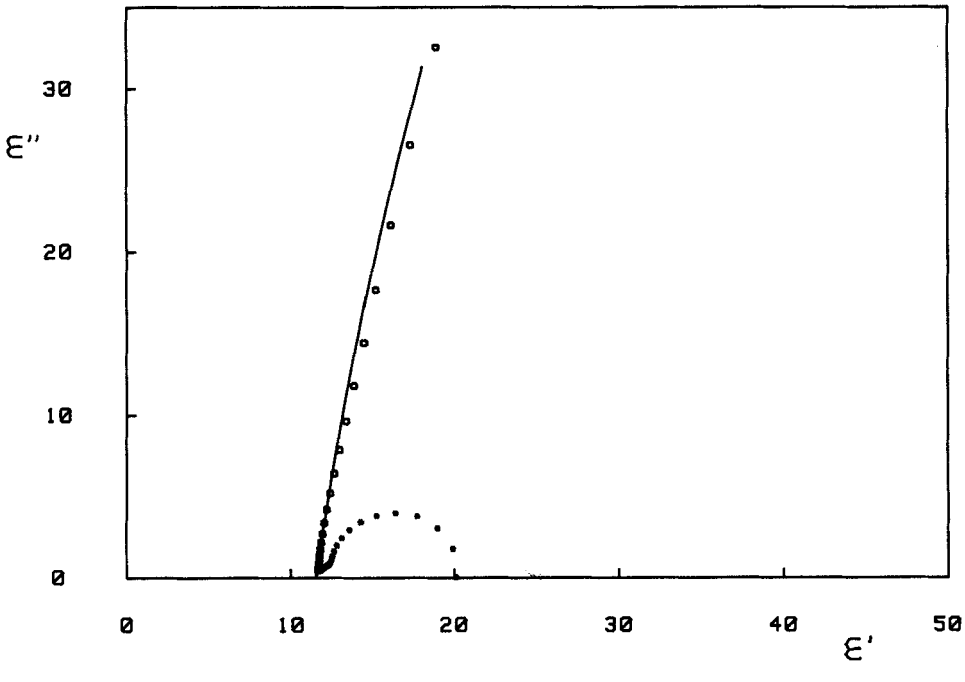
3. Results

As we shall show later, the dielectric response of the compound has a contribution in the S_C^* phase which cannot be attributed either to the Goldstone or to the soft mode and which can be resolved from both. This behaviour has been also observed by other authors [8, 9] but, as far as we know, no attempt has been made to characterize it in terms of its dielectric strength or its frequency. This has impelled us to perform a complete dielectric analysis with and without DC fields. First, we shall describe our results when measuring with metal electrodes. As we have mentioned, this cell has the advantage of no relaxational behaviour at least in the frequency range under study, and thus the measured losses can be fully assigned to the imaginary component of the dielectric permittivity, excluding that part related with the DC conduction.

Figure 2 shows the measured dielectric losses after the substraction of the DC conductivity contribution for a temperature 2·75°C below the S_C^*–S_A transition under a bias field of 4·37 kV cm^{-1}. As we shall see, this field is strong enough to quench the Goldstone mode, and thus only the soft mode contribution would be expected, except for a temperature dependent high frequency relaxation. Nevertheless, from the figure we can clearly see two different relaxations. One of them, at 260 kHz, is related with the soft mode. The other takes place at a frequency of 30 kHz and its nature seems to be unknown for the moment. This behaviour is similar to that obtained by Ozaki *et al.* [8, 9]. We have carefully analysed the contribution of these modes by the use of the Cole–Cole plots. This method has allowed us to separate their contributions by means of successive fittings to Cole–Cole functions. The process has been repeated for different bias fields and temperatures; the results can be seen in figures 3 and 4.



(*a*)



(*b*)

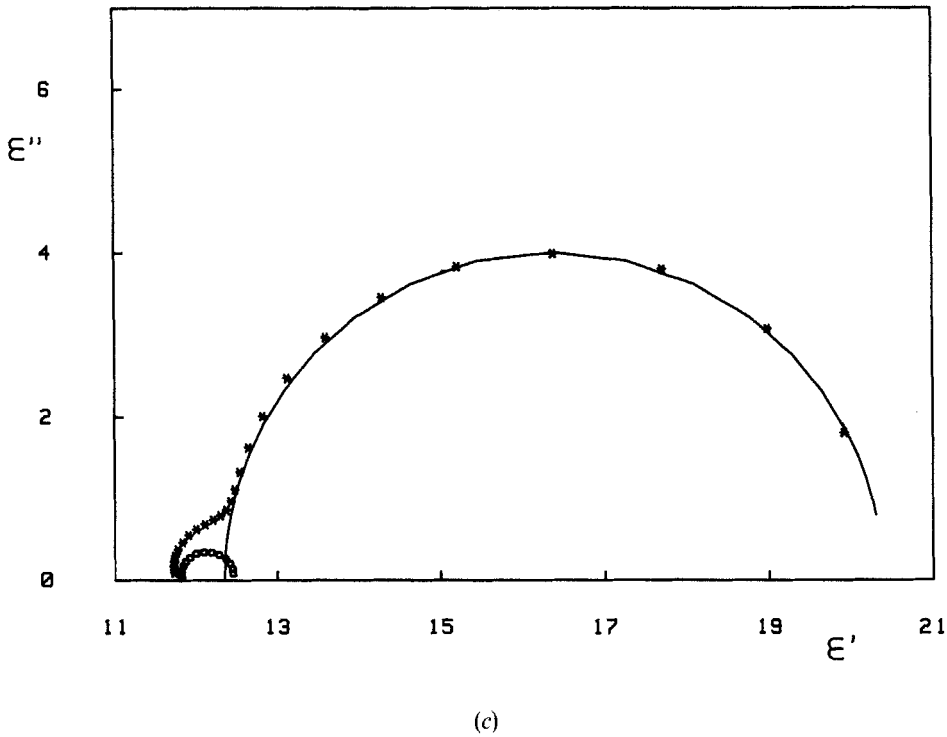


Figure 3. Deconvolution of the dielectric response at $T_{S_C^*S_A} - T = 4{\cdot}25°C$ in the S_C^* phase and at zero bias field. (*a*) Cole–Cole plot of the experimental data (stars). Open circles show the total response without the contribution of DC conduction. Solid line represents the best fit of the low frequency data to a Cole–Cole function. (*b*) The contribution of the Goldstone mode is subtracted from the total response and the result, as can be observed in the next plot, corresponds to two different relaxation mechanisms. (*c*) Final deconvolution of the unidentified process (solid line) and the soft mode (open cirlces) contributions.

3.1. S_C^* *phase with zero DC field*

In figure 3 (*a*) the stars correspond to the Cole–Cole diagram obtained from the measurements in the ferroelectric phase at zero DC field at $T - T_{S_C^*S_A} = 4{\cdot}25°C$. The open circles represent ε'' versus ε' after substracting the DC conductivity contribution which was determined from the value of the losses at low frequency. The continuous line is the best fit to the Cole–Cole function

$$\Delta\varepsilon_G^*(\omega) = \Delta\varepsilon_G/(1 + (i\omega\tau_G)^{1-\alpha_G}), \tag{1}$$

where $\Delta\varepsilon_G$ is the dielectric strength of the Goldstone mode and $\tau_G = 1/2\pi f_G$ is the corresponding relaxation time. α_G is a parameter governing the shape of the relaxation and was found to be very small (nearly Debye-like) for all temperatures.

After substracting the Goldstone mode susceptibility from the total response, the result is represented in figure 3 (*b*). The Cole–Cole plot shows a distorted semi-circle. It was fitted to a function similar to that in equation (1) showing that it can be considered as a superposition of two different relaxation mechanisms that are represented in figure 3 (*c*). In the fitting process, in all cases, we emphasized the low frequency side. The values obtained for the relaxation frequencies of these modes and their temperature

dependence allowed us to assign that with the smallest amplitude to the soft mode. The assignment of the largest contribution to a physical mechanism needs more discussion. We shall return to this point later.

The deconvolution of the dielectric response involves a great difficulty, specially near $T_{S_C^*S_A}$ because both the dielectric strength and the relaxation frequency of the different modes are very similar. This fact makes our deconvolution process valid only up to 1°C below the phase transition. Well below this point an additional problem arises because the dielectric strengths of the Goldstone and unidentified modes largely prevail over the soft mode amplitude. For instance, in the case represented in figure 3, the soft mode amplitude is three and two orders of magnitude smaller than those of the Goldstone and unidentified mode, respectively. Nevertheless, in our material the soft mode strength is large enough to allow us to characterize it up to 10°C below $T_{S_C^*S_A}$ without unwinding the helical structure by a DC field. To the best of our knowledge this characterization of the soft mode relaxation in the undisturbed S_C^* phase could be the first reported [15].

3.2. S_C^* *with a bias field*

When a bias field strong enough to unwind the helical structure is applied parallel to the smectic layers, the Goldstone mode becomes quenched and some of the problems mentioned previously can be avoided. In fact this is the usual way followed by other authors to study the soft mode in the S_C^* phase. Figures 4 (*a*) and (*b*) show the Cole–Cole diagrams at $T_{S_C^*S_A} - T = 4{\cdot}25$°C. In figure 4 (*a*) we have represented the data as they were directly measured (stars) and after substracting the DC conductivity contribution (open circles). There we can see the existence of two overlapped processes, i.e. at this temperature two modes are contributing to the dielectric constant. As before, assuming a Cole–Cole behaviour for the strongest contribution it was possible to perform the deconvolution. The continuous line is the fit to the Cole–Cole function and in figure 4 (*b*) we have represented the remaining response. This deconvolution allowed us to obtain the frequency and the amplitude of both modes as well as their temperature dependence. As before, in the fitting process we have emphasized the low frequency side.

The temperature dependence of the frequency allowed us once more to assign that with the largest amplitude to the unidentified mode and the other with the soft mode. The latter shows a critical slowing down both in strength and frequency close to $T_{S_C^*S_A}$, whereas the frequency of the unidentified mode is practically temperature independent. When studying the behaviour of both modes near $T_{S_C^*S_A}$ similar considerations to the case of no applied field must be made: both modes are completely overlapped and so it is very difficult to separate their contributions. Comparing figures 3 and 4 we can observe that the amplitude of both modes is not substantially affected by the application of a bias field. Nevertheless, as we shall show below, their frequencies are changed.

3.3. S_A *phase with and without DC field*

Cole–Cole diagrams of the measured dielectric response in the S_A phase are shown in figure 5. There we can see only one relaxation which is related to the soft mode. The large dielectric strength of this mode in our material allowed us to characterize it over a

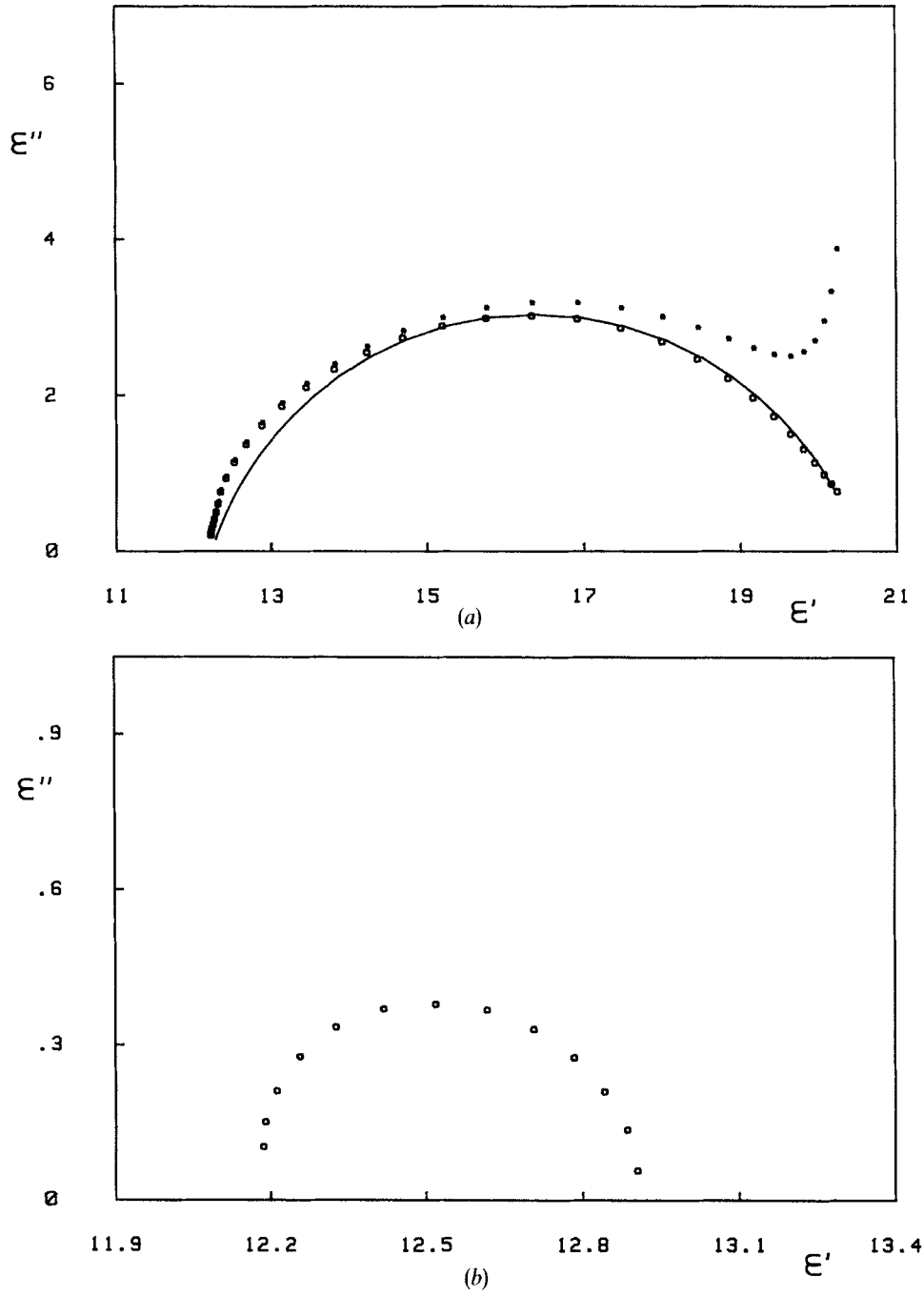


Figure 4. Deconvolution of the dielectric response at $T_{S_C^* S_A} - T = 4{\cdot}25°C$ in the S_C^* phase and at 4·37 kV cm^{-1} bias field perpendicular to the helix axis. (*a*) Stars: Cole–Cole diagram of the measured data. Open circles: Cole–Cole diagram after the subtraction of the DC conduction. Solid line represents the best fit of the low frequency data to the Cole–Cole function. (*b*) In the last step we subtract the contribution of the unidentified mode. Open cirlces represent the remaining contribution to the dielectric constant; i.e. the soft mode contribution.

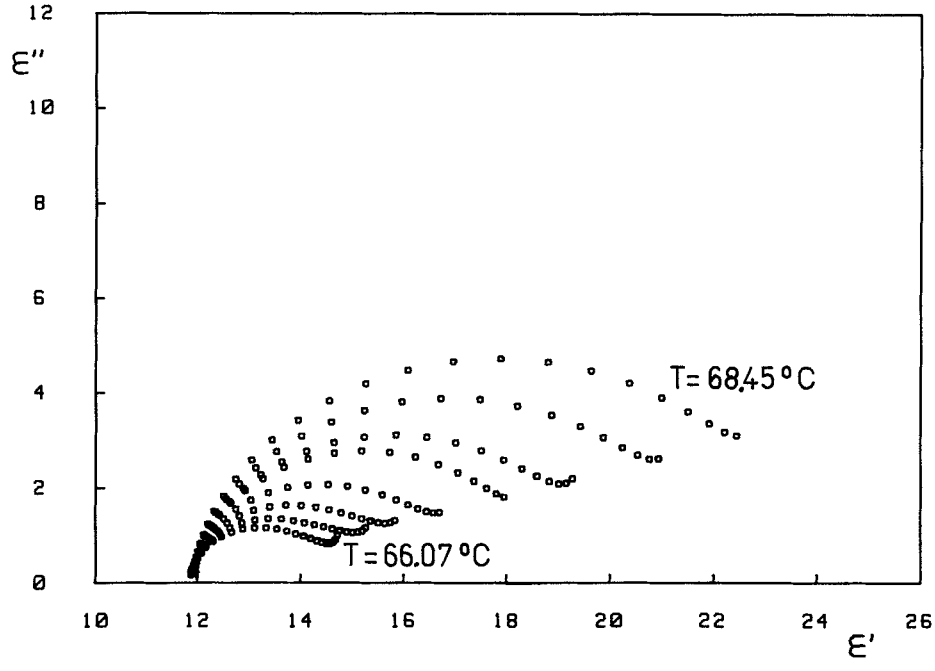


Figure 5. Cole–Cole diagrams of the measured dielectric response at different temperatures in the S_A phase.

broad temperature range, up to 10°C above the phase transition. In this phase and in total accord both with the predictions of Landau theory and with the results of other authors [4, 16], the strength and frequency are not found to be greatly affected by the bias field, except for a very narrow range of about 1°C above $T_{S_C^* S_A}$.

4. Discussion

The additional mode, which takes place at 30 kHz with no field, and at 1 kHz with an applied field, was only found in the ferroelectric phase. There, its frequency and strength are almost temperature independent. To be sure that this mode is not intrinsically related with the helical structure, a detailed study of the dependence of the frequency and amplitude of the Goldstone mode with the bias field was carried out. In figure 6, the open circles represent the field dependence of the dielectric permittivity at 100 Hz. It decreases smoothly as the field increases for low fields, but when the field is higher than 0·5 kV cm^{-1} the dielectric permittivity exhibits an abrupt drop. From a field slightly higher than this, the permittivity remains constant, being the value related with the high frequency modes. Then, we can assume the helix to be completely unwound.

The stars in figure 6 show the field dependence of the frequency of the Goldstone mode. Its behaviour is very similar to that found for the amplitude. For fields smaller than the critical one the frequency remains constant at about 500 Hz. For higher fields this frequency decreases sharply and from a field of about 0·6 kV cm^{-1} the losses, and then the associated relaxation process, disappear, which confirms the quenching of the Goldstone mode.

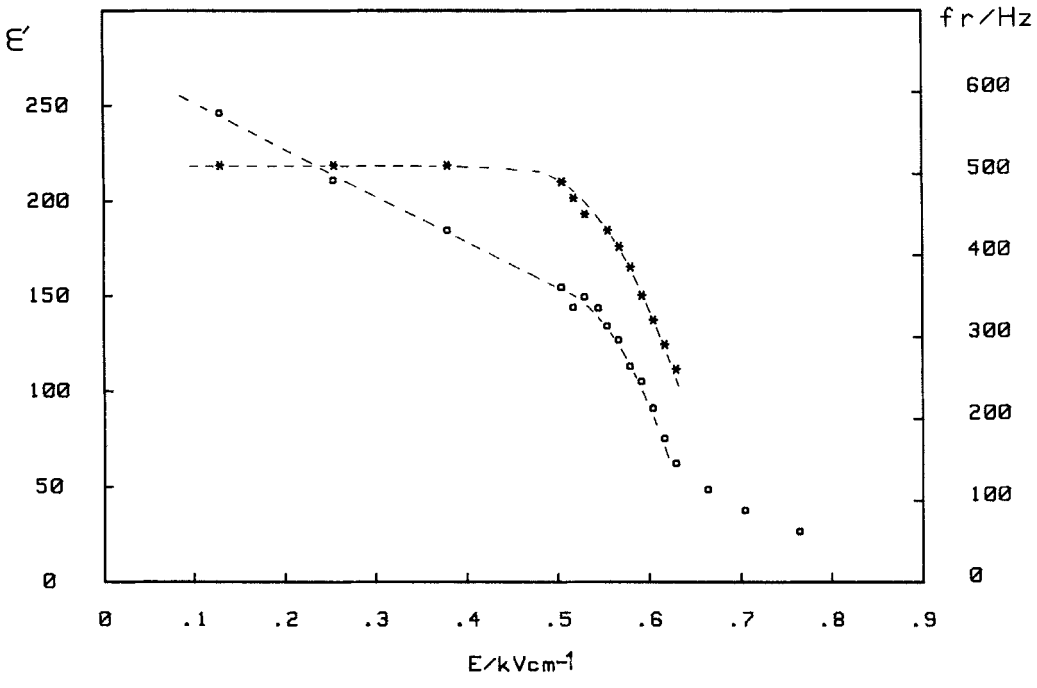


Figure 6. Open circles: DC field dependence of the dielectric permittivity at 100 Hz. Stars: relaxation frequency of the Goldstone mode versus applied DC electric field. The relaxation frequency remains constant up to 0·5 kV cm^{-1}. Both plots correspond to $T_{S_C^*-S_A} - T = 2{\cdot}75°C$. The dashed lines are included as a guide to the eye.

In our opinion these sets of data confirm that the unidentified mode, which was also observed with a field as high as 4·37 kV cm^{-1}, much higher than the critical one, cannot be attributed to any intrinsic effect of the helical structure. As we have mentioned before, all of the measurements were performed with metal electrodes and without any surface treatment to align the planar structure. In order to clarify the nature of this unexpected dielectric contribution we repeated the whole study using two kinds of cells with ITO coated glass electrodes. One of them was coated with nylon 6/6 to achieve planar alignment whereas the other one received no surface treatment. In both cases optical observations allowed us to check the alignment state. Measurements performed with the poorly aligned, but planar, cell are similar to those obtained with the cell with metal electrodes, showing three contributions in the S_C^* phase and one in the S_A. However, with the well aligned sample, only two contributions were found in the S_C^* phase. The behaviour of their frequencies with temperature allowed us to assign them to the Goldstone and soft modes, respectively. These results suggest that the unidentified mode is due to the defect structure related with different directions of the helical axis in poorly aligned planar samples with a domain structure. This behaviour is similar to that present in solid ferroelectrics in a multidomain state, where relaxations associated with movements of the domain walls are frequently observed [17]. Now let us return to the study with the metal electrodes.

In figure 7 we plot the relaxation frequencies of the three modes versus temperature at zero and 4·37 kV cm^{-1} fields (all of the symbols are explained in the figure). In the S_A

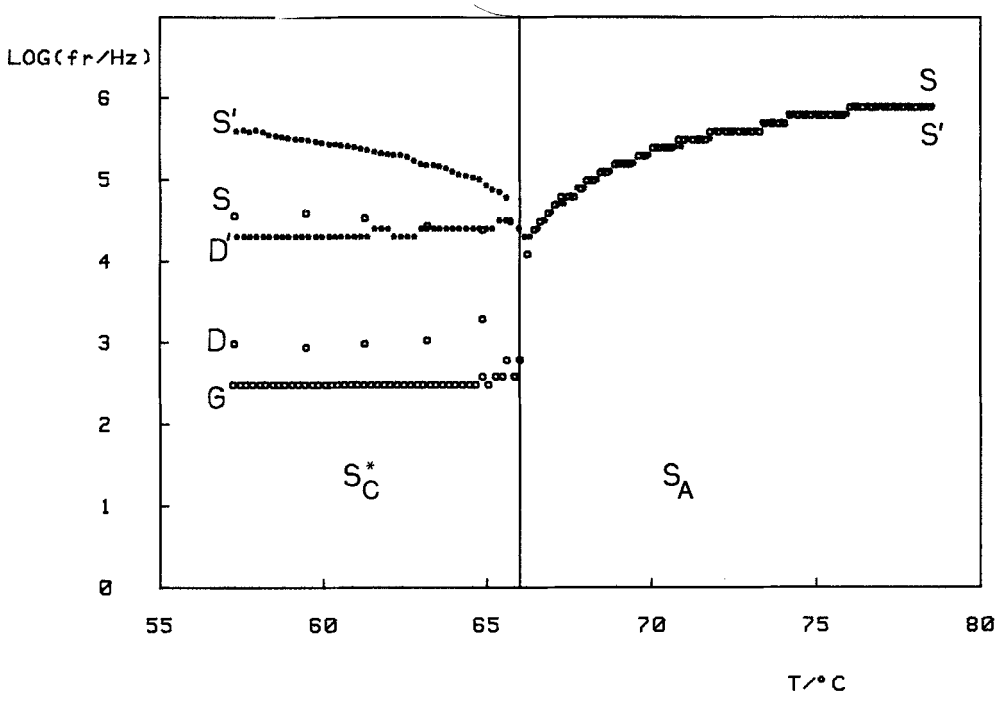


Figure 7. The temperature dependence of the relaxation frequencies of the different processes, under a 4·37 kV cm^{-1} DC field (dots) and with no applied field (open circles). The transition temperature (solid line), $T_{S_C^*S_A}$, was determined from the maximum of the soft mode strength. (S: soft at $E=0$; S': soft at $E=4{\cdot}37$ kV cm^{-1}; G, Goldstone; D, defects contribution at $E=0$; D', defects contribution at $E=4{\cdot}37$ kV cm^{-1}).

phase the behaviour of f_S near $T_{S_C^*S_A}$ is in good agreement with the predictions of Landau theory. Moreover, this frequency is not affected by the bias field. However, our measurements do not allow us to obtain any conclusion about the effect of the field very close to $T_{S_C^*S_A}$. In the S_C^* phase three modes were found at zero DC field and two under the bias field. Although the behaviour of f_S with temperature is that expected, in the figure we can see that it is strongly affected by the bias field. When studying the soft mode in this phase most authors assume that there is no noticeable difference between the true soft mode contribution and that obtained under a bias field, and so take the latter as the soft mode contribution. Our measurements of the soft mode at zero field may have a noticeable uncertainty because of the deconvolution process and the amplitude differences of the contributions, but in no case are the observed differences drowned in the error. For example, Gouda [18] estimated this difference could be about 15 Hz for standard values of the elastic constants and pitch. The results in our study show this kind of assumption must be taken more carefully from now on.

This work was supported by the CICYT, Comisión Interministerial de Ciencia y Tecnología, of Spain, grant No. MAT88-0324-C02-02.

References

[1] LEVSTIK, A., CARLSSON, T., FILIPIC, C., LEVSTIK, I., and ZEKS, B., 1987, *Phys. Rev. Lett.*, **35**, 3527.

[2] PAVEL, J., GLOGAROVÁ, M., and BAWA, S. S., 1987, *Ferroelectrics*, **76**, 221.

[3] EZCURRA, A., PÉREZ JUBINDO, M. A., DE LA FUENTE, M. R., ETXEBARRIA, J., REMÓN, A., and TELLO, M. J., 1989, *Liq. Crystals*, **4**, 125.

[4] GOUDA, F., ANDERSSON, G., LAGERWALL, S. T., SKARP, K., STEBLER, B., CARLSSON, T., ZEKS, B., FILIPIC, C., and LEVSTIK, A., 1989, *Liq. Crystals*, **6**, 219.

[5] LEGRAND, C., and PARNEIX, J. P., 1990, *J. Phys., Paris*, **51**, 787.

[6] CARLSSON, T., ZEKS, B., FILIPIC, C., and LEVSTIK, A., 1990, *Phys. Rev.* A, **42**, 877.

[7] BIRADAR, A. M., WRÓBEL, S., and HAASE, W., 1989, *Phys. Rev.* A, **39**, 2693.

[8] OZAKI, M., HATAI, T., and YOSHINO, K., 1988, *Jap. J. appl. Phys.*, **27**, L1996.

[9] OZAKI, M., NAKAO, K., HATAI, T., and YOSHINO, K., 1989, *Liq. Crystals*, **5**, 1219.

[10] VALLERIEN, S. U., KREMER, F., KAPITZA, H., ZENTEL, R., and FRANK, W., 1989, *Phys. Lett.* A, **138**, 219. Although authors do not mention this fact, in figure 2 three relaxation processes are presented in the S_C^* phase.

[11] SIERRA, T., MELÉNDEZ, E., SERRANO, J. L., EZCURRA, A., and PÉREZ JUBINDO, M. A., 1991, *Chem. Mater.*, **3**, 157.

[12] DE LA FUENTE, M. R., EZCURRA, A., PÉREZ JUBINDO, M. A., and ZUBIA, J., 1990, *Liq. Crystals*, **7**, 51.

[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] CAVA, R. J., PATEL, J. S., COLLEN, K. R., GOODBY, J. W., and RIETMAN, E. A., 1987, *Phys. Rev.* A, **35**, 4378.

[15] It must be noted that the authors of [1] already used a deconvolution technique to separate the two modes (Goldstone and soft mode) at one fixed temperature inside the S_C^* phase very close to the phase transition. Nevertheless they did not characterize and obtain the frequency and strength of the soft mode well inside the S_C^* phase as a function of temperature without unwinding the helix in the ferroelectric phase.

[16] GLOGAROVÁ, M., and PAVEL, J., 1989, *Liq. Crystals*, **6**, 325.

[17] DE LA FUENTE, M. R., PÉREZ JUBINDO, M. A., SOLIER, J. D., and MAÑAS, J., 1984, *Ferroelectrics*, **54**, 77.

[18] GOUDA, F., ANDERSSON, G., CARLSSON, T., LAGERWALL, S. T., SKARP, K., STEBLER, B., FILIPIC, C., ZEKS, B., and LEVSTIK, A., 1989, *Molec. Crystals liq. Crystals Lett.*, **6**, 151.