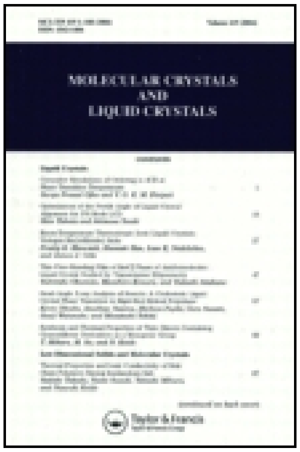


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Dielectric Properties of Nematic and Ferroelectric Liquid Crystals

H. J. Müller [a] & S. Jayaraman [a]

[a] Departamento de Física, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, SC, Brasil

To cite this article: H. J. Müller & S. Jayaraman (1998): Dielectric Properties of Nematic and Ferroelectric Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 309:1, 93-110

To link to this article: http://dx.doi.org/10.1080/10587259808045521

*Mol. Cryst. Liq. Cryst.*, 1998, Vol. 309, pp. 93–110
Reprints available directly from the publisher
Photocopying permitted by license only

# Dielectric Properties of Nematic and Ferroelectric Liquid Crystals

H. J. MÜLLER and S. JAYARAMAN

*Departamento de Física – Universidade Federal de Santa Catarina – 88040-900 – Florianópolis, SC, Brasil*

*(Received 7 January 1996)*

Different contributions to the dielectric permittivity in two different ferroelectric liquid crystal materials are studied, with emphasis on the Soft mode and the Golstone mode. Also in three nematic liquid crystals, the dielectric permittivity was studied as a function of temperature and frequency. Experimentally, the complex dielectric permittivity was studied as a function of temperature in the frequency range 5 Hz–13 MHz. The Soft mode dielectric behavior was studied as a function of frequency and bias electric field. In the smectic C*, I*, and J* phases, the frequency dependence of the dielectric contribution of the Golstone mode was measured.

*Keywords:* Ferroelectric; dielectric constants; X-ray studies

## INTRODUCTION

Ferroelectric liquid crystals (FLC) were theoretically discovered by R. B. Meyer [1] and the first substance with ferroelectric properties (DOBAM BC) was synthesized in 1975 [2]. Then a large number of ferroelectric liquid crystals were synthesized with a greater chemical and thermal stability and with a large number of ferroelectric smectic phases. The first use of FLC in displays using the surface stabilization concept [3] was to follow only in 1980. Using surface-stabilized ferroelectric liquid crystals displays (SSFLQD) various devices [4, 5] such as flat-panel screens for video and data graphic application and high-speed shutters, have been developed.

We investigated the chiral smectic phases SmA*, SmC*, SmI* and SmJ* and we disucss the relaxation frequency of the systems when the electric field is applied parallel to the smectic layers. We observe the behavior of the two modes connected with reorientational movement of the director: a) The Soft mode, which is due to the variation of the amplitude of the angle of inclination of the molecules (tilt angle fluctuations), has a relaxation frequency $f_S$ which depends on temperature and is of the order of kHz–MHz; b) The Golstone mode, which is due to the variation of the direction (phase) of the tilt angle of the molecules (phase fluctuations), has a relaxation frequnecy of the order of a few Hz to 100 kHz (6, 7, 8) and is practically constant with temperature.

In the SmA* phase, only the Soft mode appears. In the tilted smectic phases like the SmC*, SmI* and the SmJ*, the Soft mode as well as the Golstone mode appears. The Golstone mode is more intense than the Soft mode. However, the Soft mode could be observed experimenteally, applying an additional electric field (Bias) which breaks the helicoidal structure and thus eliminates the effect of Golstone mode. When a system, in all these diverse phases, is deformed and subsequently the cause of the deformation removed, the system returns to the initial state with a characteristic relaxation time depending on the elasticity and viscosity of the phase. The properties, along with the spontaneous polarization, angle of tilt, wavelength of helice (pitch) are of greater importance to the technical applications such as electro-optical devices. One of those parameters important in application could be determined by dielectric measurements and the measurement of dielectric anisotropy. In this work we measure the contribution of Soft mode in SmA* phase and Golstone mode in tilted smectic phases as a function of frequency at various temperatures.

For non-chiral liquid crystals, the study of dielectric permittivity is also interesting from the point of view of basic research as well as application. It is possible to obtain information about the dipolar order in the nematic, SmA* and SmC* phases. The behaviour of the dielectric relaxation provides information on the possible molecular movements about the longitudinal and the transverse axes. The dielectric anisotropy $\Delta\varepsilon$ is more important for application in technology in digital displays, because the magnitude of this value influences the speed of the optical transition, whereas, the sign governs the cell geometry to achieve the desired effect. Thus, previous researchers have sought to measure and understand the dielectric properties of nematic phases [10, 11, 12].

To obtain the real ($\varepsilon'$) and the imaginary ($\varepsilon''$) part of the complex dielectric constant, we measured the capacitance C and the conductance G of the sample. The values of C and G are transferred to a computer which, through a proper program calculate the values of $\varepsilon'$ and $\varepsilon''$. The value of $\varepsilon'$ is equal to $C_D/C_0$, where $C_D$ is the value of the capacitance measured with a cell ffilled with liquid crystal, value corrected for parasitic capacitance ($C_D = C - C_x$) where C is the value of the measured capacitance and $C_x$ is the contribution of the parasitic capacitance; $C_0$ is the value of the capacitance of the vacant cell.

$\varepsilon'' = G/2\pi f C_0$ where $f$ is the frequency is the frequency of the electric field. To determine the Debye relaxation [13], the values of Real and imaginary part of $\varepsilon^* = \varepsilon' - j\varepsilon''$ depend on the frequency as follows:

$$\varepsilon'(f) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/[1 + (f/f_R)^2] \text{ and } \varepsilon''(f) = (\varepsilon_0 - \varepsilon_\infty)/[1 + (f/f_R)^2]\cdot(f/f_R)$$

where $f_R$ is the relaxation frequency, where $f_R = f_G$ or $f_S$ in the case of Golstone or Soft mode and $\varepsilon_0$ is the dielectric constant before the relaxation and $\varepsilon_\infty$ is the dielectric constant after the relaxation.

## MEASUREMENTS OF $\varepsilon_\parallel$, $\varepsilon_\perp$ AND $\Delta\varepsilon$

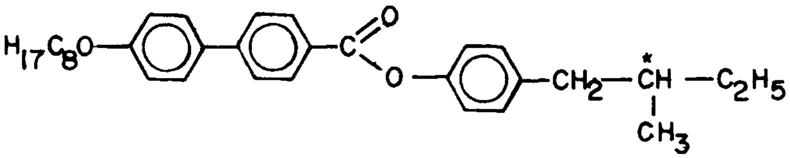
The capacitances and conductances were measured using a HP4192A impedance analyser (5 Hz–13 MHz). The cell consist of two laminars of conducting glass (ITO) spaced with mylar of thickness 36 µm, in the planar as well as the homeotropic orientaion. the capacitance $C_0$ of the vacant cell was measured as a function of temperature and as a function of frequency. It was verified that at room temperature, the capacitance was practically constant up to 1 MHz and at 7 kHz, the capacitance was constant from room temperature up to 150°C.

To obtain $\varepsilon_\parallel$ the measurements of C were done without any surface treatment, because all the compounds showed a natural tendency to orient homeotropically. A magnetic field of about 9 kG resulted in a better orientation. The cell is filled with capillary action by heating the sample upto the isotropic phase. the temperature is reduced slowly, from the isotropic phase, *with 0.5°C/min*, using a temperature regulator with a platinum resistence. The orientation is verified by observing the sample with crossed polarisers. The planar alignment (for obtain $\varepsilon_\perp$) is more difficult. In this case, the layers are perpendicular to the capacitor plates. The surface was treated with dilute polivinyl alcohol and the surface was duly frictioned, then the cell as filled, cooled slowly from the isotropic phase in a magnetic field around 0.9 T. The quality of orientation is verified using crossed polarisers and also through quality of measurements of the electric parameters during the orientation process. This orientation process is analogous to those described in other articles [8, 14, 16].

The X-ray diffractometric measurements were performed using a focusing, horizontal, two circle X-ray diffractometer STOE Stadi2 with a modified oven to asses the temperature dependent scattering data. The X-ray source was a long fine focus X-ray tube (Siemens FK). The Cuk$_\alpha$ radiation ($\lambda = 1.54056$ A) was focused by a curved Ge(111) monochromator. The mechanically and electrically controlled smallest step width of the diffractometer in the $2\theta$ and $\omega$ was 0.001. For the fast diffractometer, a detector is used with a resolution of the step width 0.01 in $2\theta$. The temperature stability at the sample location in the range of 30°C to 230°C is 0.01°C.

The follwing substance were investigated;

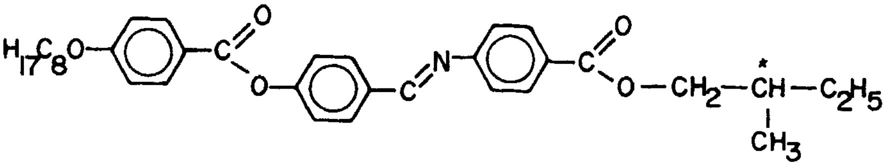
1) 4-(2-ethylbutyl) phenyl-4'-(octyloxy)-(1,1')-biphenyl-4-carboxylate (8OSI), has the following structural formula



with the mesophases (Temperature in °C)
I-171.8-Bp-171.6-Ch-167-SmA*-130.8-SmC*-78.7-SmI*-74-SmJ*-51-SmK.

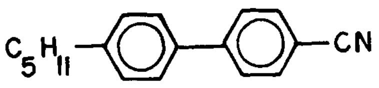
This compound exhibits three ferroelectric liquid crystalline phases: SmC*, SmI* and SmJ*. In the SmK* phase, it is not possible to observe the ferroelectric behaviour because of the very strong intermolecular correlations.

2) *p*-octaloxybenziloxy-*p*-benzilidene-*p*-2-methylpenthyl-carboxyanilina (FeC8)
with the structural formula



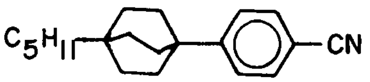
and with the phases (temperature in°C)
Solid-98-SmC*-124-SmA*-183-Ch-195-Bp-195.2-I.

3) 4'-*n*-pentyl-4-cyanobiphenyl (CB5)
with structural formula



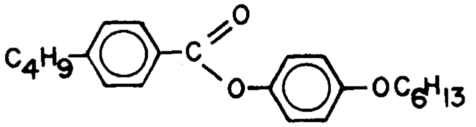
and with a nematic phase, Solid - 22.5 - N - 34.5 - I (Temperature°C).

4) 4(4′-pentyl-(2.2.2)-bicyclooctyl-benzonitril (BCO)
with structural formula



and with a nematic phase, Solid - 62 - N - 100 - I (Temperature in °C).

5) 5-*n*-butylbenzoacid - (4′ - *n* - hexaloxyphenyl) - esther
with structural formula



and with a nematic phase, solid - 31 - N - 48.5 - I (Temperature in °C).
The compound Fec8 was synthesized in UFSC and the others were supplied by E. Merck Company.

## EXPERIMENTAL RESULTS

### 1) Ferroelectric Compound 80SI

The Figure 1 shows the temperature dependence of the dielectric anisotropy of the ferroelectric compound 80SI in the smectic phases, C*, I* and J* at frequency of 7 kHz. The anisotropy is negative indicating a strong component of transverse electric dipole. In the smectric-C phase, near the transition to the smectic-A phase, the perpendicular component of dielectric constatnt ($\varepsilon'$) decreases considerably, the spontaneous polarization disappears, and the tilt angle of the director decreases, as shown by the results of X-ray studies, Figure 2. The variation of perpendicular component of the dielectric constant $\varepsilon'$ and the dielectric absorption $\varepsilon''$ of the compound 80SI in the SmC* phase at temperature of 120°C is shown in the Figure 3. We can note that

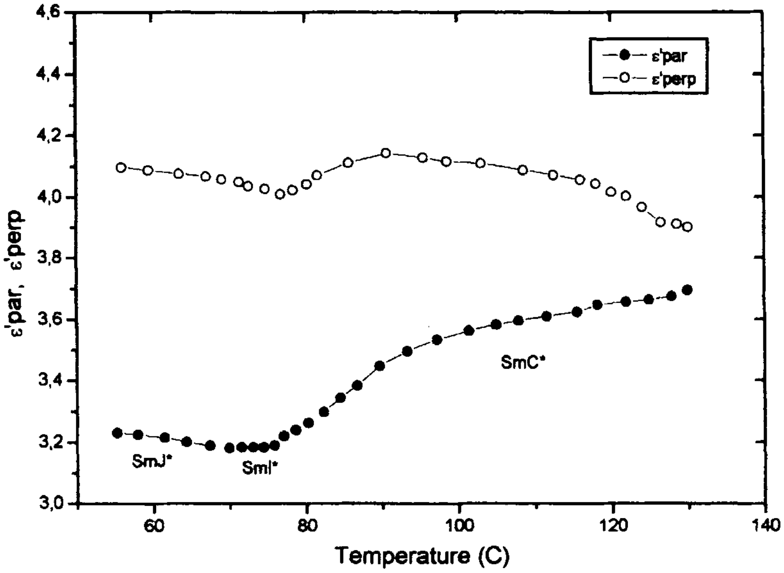


FIGURE 1 Dielectric anisotropy as a function of temperature for the compound S180 at $f = 7$ kHz frequency in the SmC*, SmI*, SmJ* phases-S180AN.

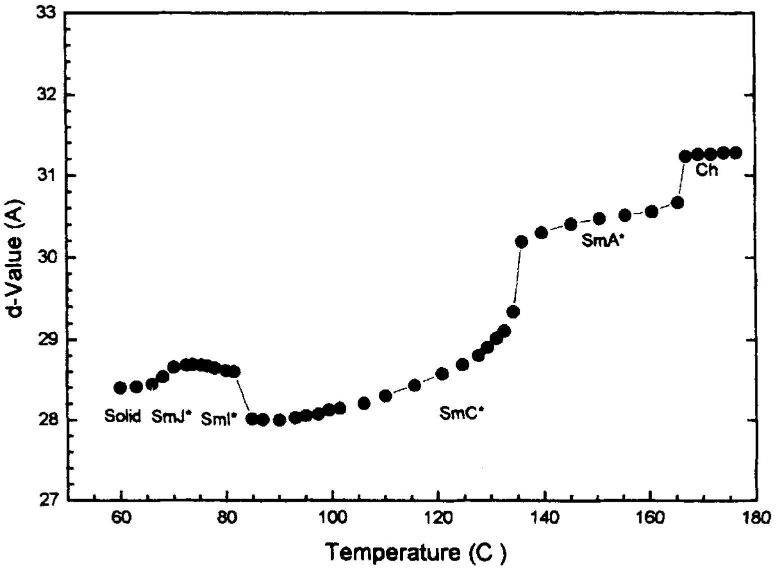


FIGURE 2 The *d*-Value vs temperature for 80SI with smectic A*, C*, I*, J* phases.

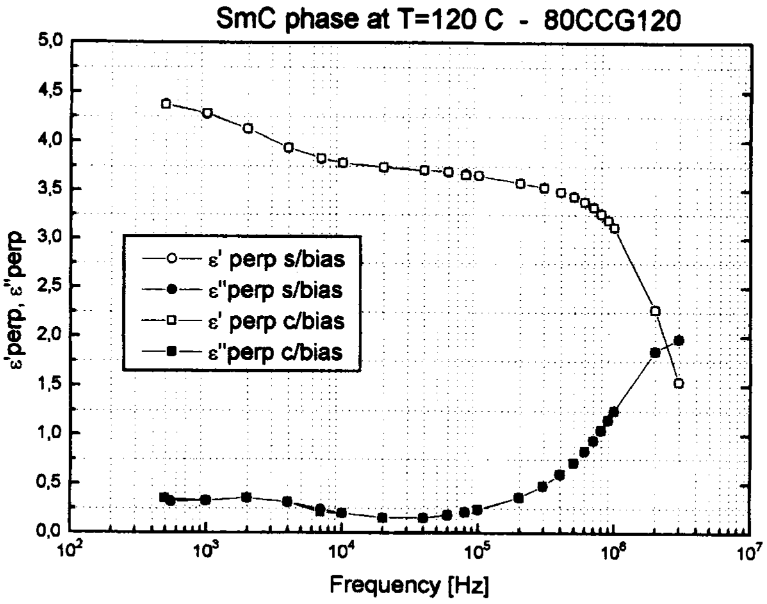


FIGURE 3 Frequency dependence of the dielectric constant ε'perp and dielectric loss ε"perp of the compound 80SI in the SmC phase at $T = 120$ C-80CCG120.

the dielectric relaxation process is due to the Goldstone mode which is centered at a frequency of $2.10^3$ Hz. Applying an additional electric field, bias of 20 volts, we observe very little change in relation to absence of bias, probably due to a small spontaneous polarization. For a more ordered smectic phase. SmI*, Figure 4, we observe a contribution of Goldstone mode, but in smaller intensity, in the region of $4.10^2$ Hz. The relaxation frequency in the SmI* phase is smaller than in the SmC* phase, because of the increase in viscosity. In the SmJ* phase, Figure 5, the contribution of the Goldstone mode is not observed probably due to a strong interlayer correlation. This fact was already suggested before [16] and also verified before [17]. In the smectic-A* phase, measurements were made as a function of frequency at different temperatures. We noted a slight decrease in the value of $\varepsilon'$ and $\varepsilon''$ with increase of temperature, concentrating on the soft mode at a frequency of $2.10^6$ Hz. by constructing Cole–Cole diagrams (18) i.e., by plotting the imaginary part of the complex dielectric constant as a function of the real part, we expect to get a semicircle of only one relaxation mechanism present. If two or more relaxation mechanisms are interacting we instead expect a distorted semicircle. In Figure 6, we show a sequence of Cole–Cole diagrams for some different temperatures and the smectic phases C*, I* and J*

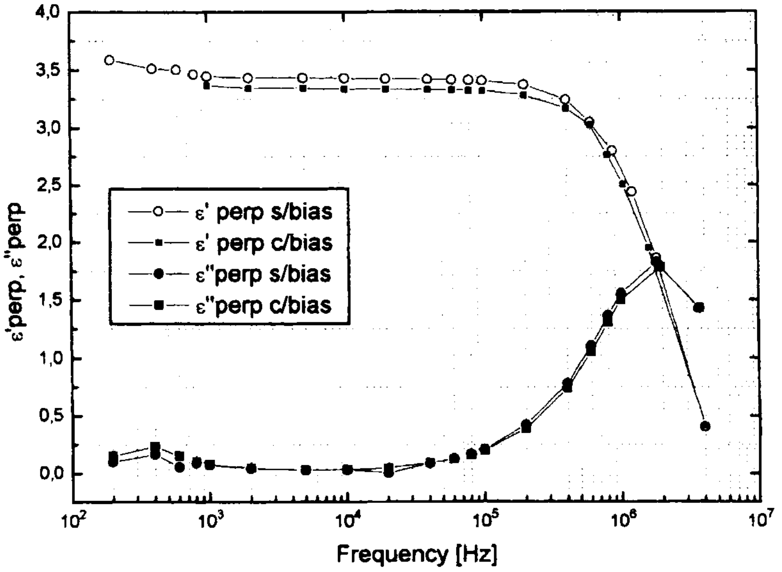


FIGURE 4 Frequency dependence of the dielectric constant ε'perp and dielectric loss ε''perp of the compound 80SI in the SmC phase at $T = 75$ C-80ICG75.

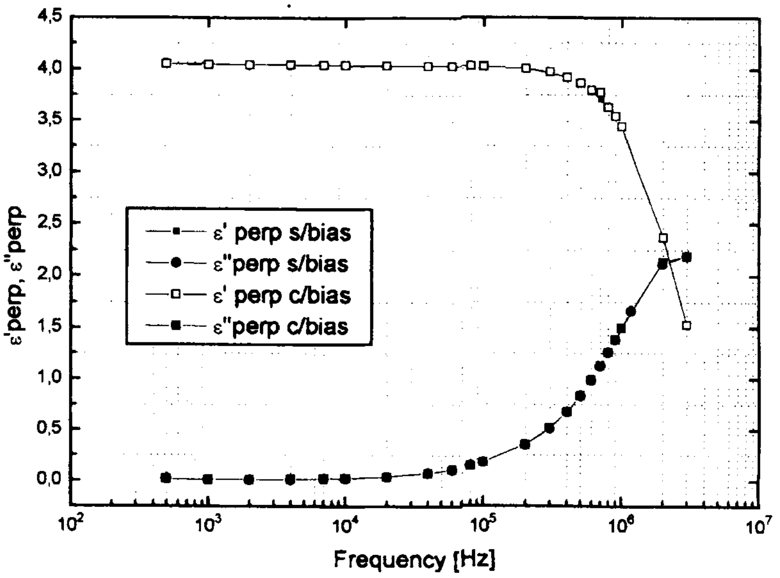


FIGURE 5 Frequency dependence of the dielectric constant ε'perp and dielectric loss ε''perp of the compound 80SI in the SmJ phase at $T = 65.4$ C-80JC654.

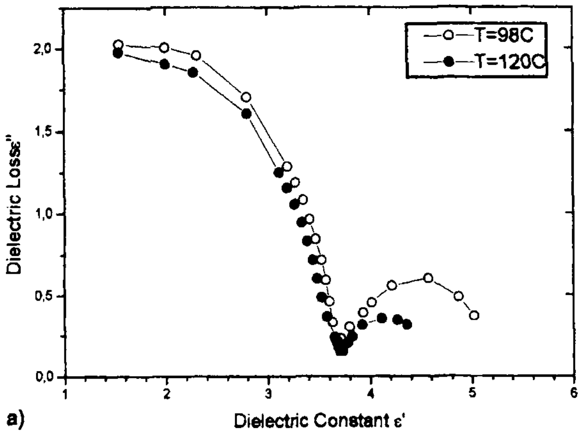


FIGURE 6a Cole–Cole plots for the Golstone mode at different temperature of Smectic C phase-80SiCCOL.

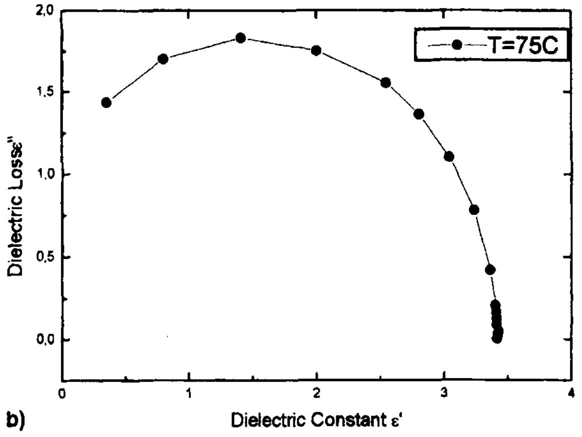


FIGURE 6b Cole–Cole plots for the Golstone mode at different temperature of Smectic I phase-80SiICOL

we observe that the curves are not exactly semicircular. The reason may be due to the absence of perfect alignment, which create a defect structure.

## 2) Ferroelectric Compound FeC8

Figure 7 shows the variation of dielectric anisotropy with temperature of the ferroelectric compound FeC8 for a frequency of 7 kHz. The anisotropy is negative and the modulus of anisotropy decreases with temperature; the

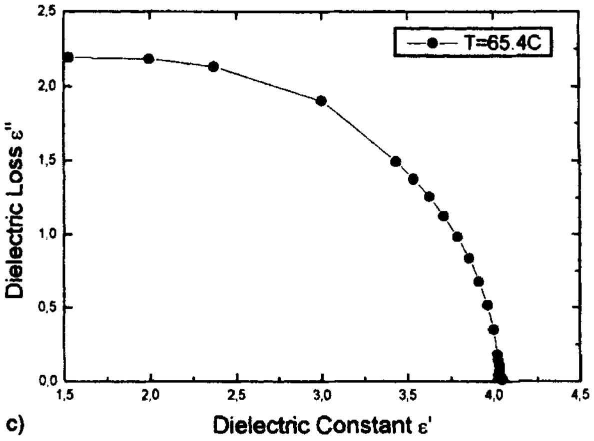


FIGURE 6c Cole–Cole plots for the Golstone mode at different temperature of Smectic J phase- 80SiJCOL.

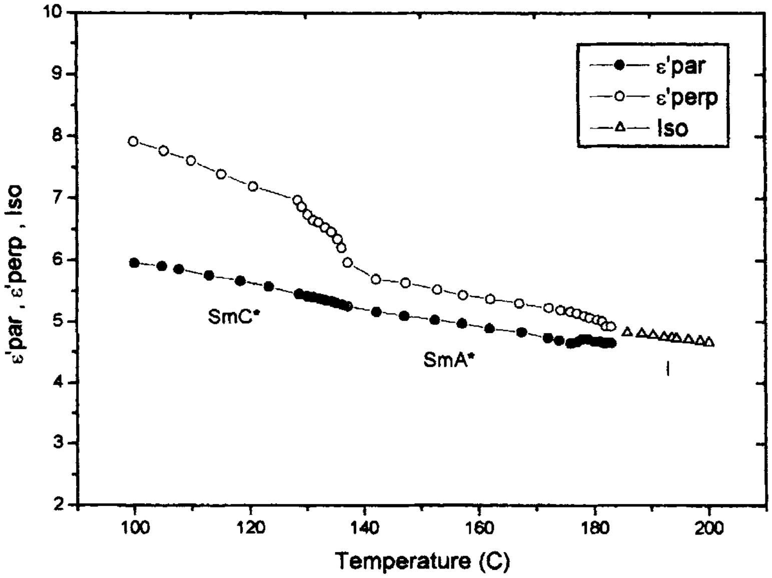


FIGURE 7 Dielectric anisotropy as a function of temperature for the compound FeC8 at $f = 7$ kHz frequency in the SmC*, SmA* and N phases-FEC8AN.

spontaneous polarisation disappears and the tilt angle of the layers also decreases, as observed with X-ray studies in Figure 8. The anisotropy is approximately constant in the SmA* phase and is expected because of the proportionality between the order parameter and the dielectric anisotropy.

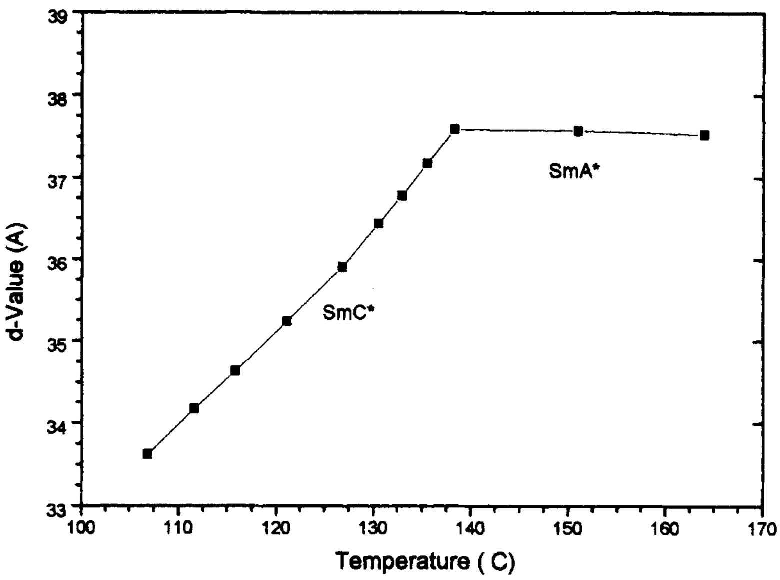


FIGURE 8 The *d*-value vs temperature for FeC8 with smectic C*, A* and N phases.

In the SmA* phase, Figure 9, is shown that the Soft mode is localized in the region of 9.$10^5$ Hz.

### 3) Nematic Compound CB5

Figure 10 shows the dielectric anisotropy in the nematic phase of the compound CB5, with a strong positive dielectric anisotropy due to the presence of a large dipole moment along the major molecular axis ($\varepsilon_\parallel$) being about twice that in the transverse direction ($\varepsilon_\perp$). This is attributed to the nitril group as well to the arrangement in an antiparallel configuration [19, 20]. Figures 11.a and 11.b show respectively the variation of the dielectric constants ($\varepsilon'_\parallel$, $\varepsilon_\perp$) and the dielectric absorption ($\varepsilon'_\parallel$, $\varepsilon''_\perp$) as a function of frequency of the compound CB5 for different temperatures. The relaxation frequency is localized for parallel components at 2.$10^5$ Hz and for the perpendicular components at 3.$10^5$ Hz, noting very little influence temperature.

### 4) Nematic Compound CBO

Figure 12 shows the dielectric anisotropy of the nematic phase of the compound CBO, with positive dielectric anisotropy, with a value comparable to

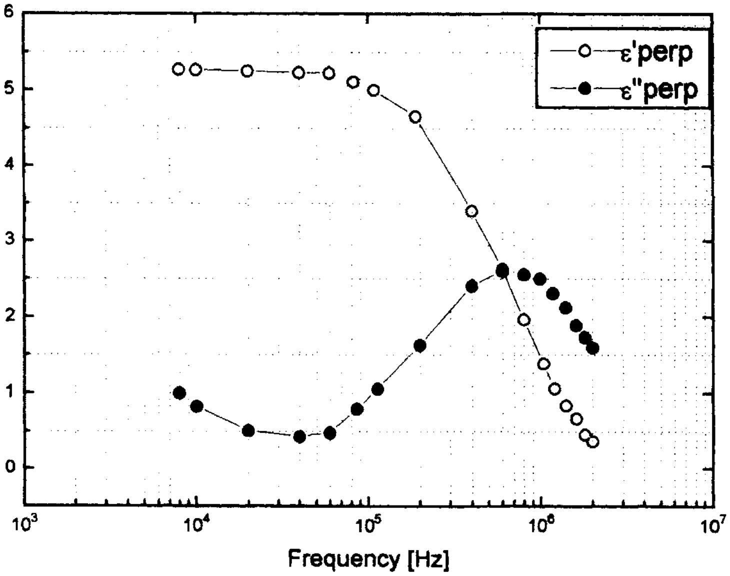


FIGURE 9 Frequency dependence of the dielectric constant ε'perp and dielectric loss ε"perp of the compound FeC8 in the SmA phase at 137 C-FE2CGF1.

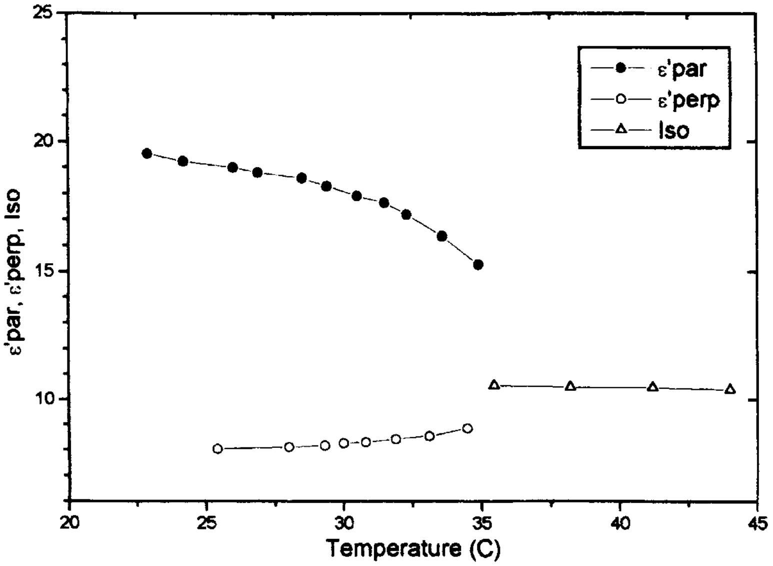


FIGURE 10 Dielectric anisotropy as a function of temperature for the compound 5CB at $f = 7$ kHz-CB5AN.

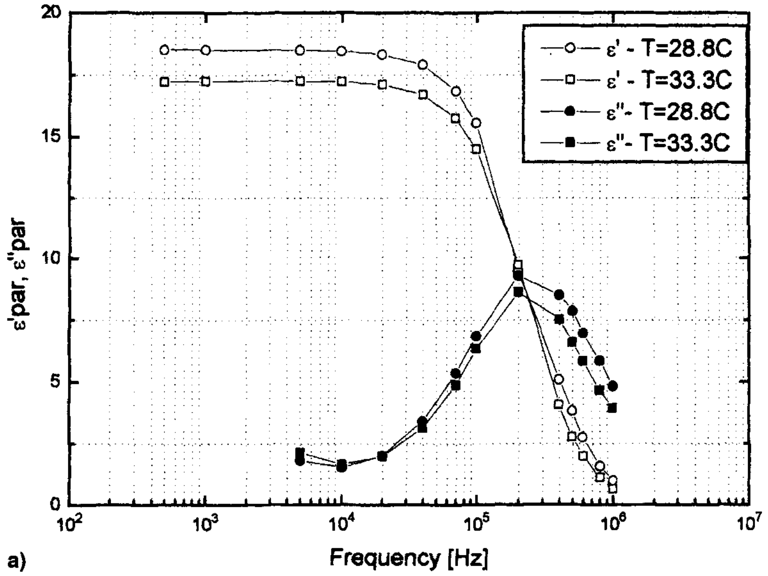


FIGURE 11a Frequency dependence of the dielectric constant ε'par and dielectric loss ε''par at different temperatures of the compound CB5-CBACGF.

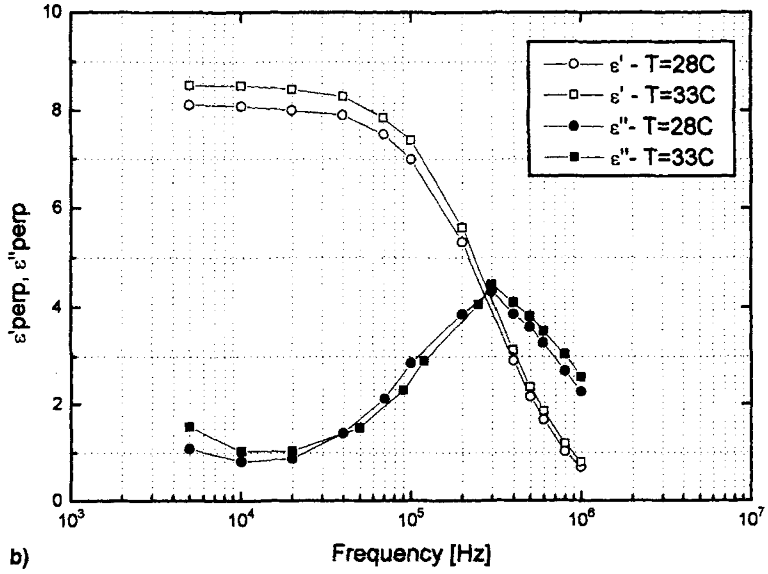


FIGURE 11b Frequency dependence of the dielectric constant ε'perp and dielectric loss ε''perp at different temperatures of the compound CB5-CBECGF.

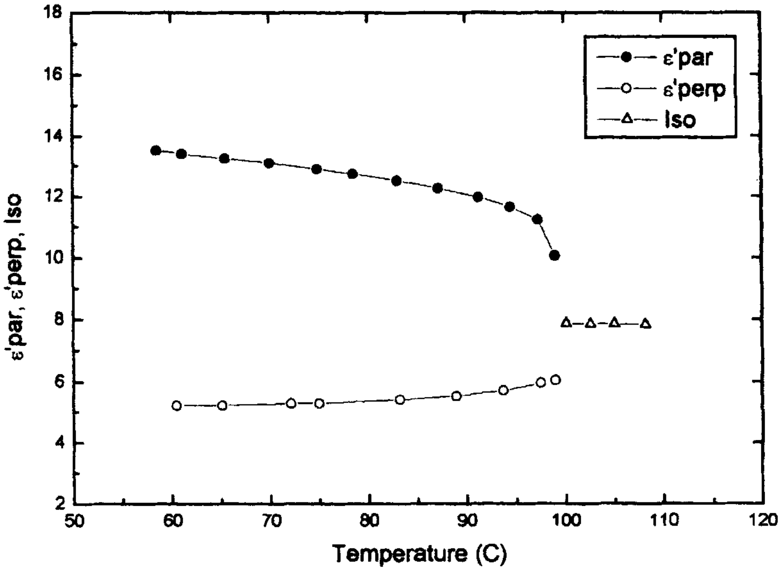


FIGURE 12 Dielectric anisotropy as a function of temperature for the compound BCO at $f = 7$ kHz-BCOAN.

the compound CB5, having an octyl ring instead of the phenyl ring. Figures 13.a and 13.b show respectively the variation of dielectric constants ($\varepsilon'_{\parallel}$, $\varepsilon'_{\perp}$) and the dielectric absorption ($\varepsilon'_{\parallel}$, $\varepsilon'_{\perp}$) as a functional of frequency of the compound CBO for different temperatures. For the parallel compounds, the relaxation frequency is localized at $3.5.10^5$ Hz and for the perpendicular components, at $4.5.10^5$ Hz, thus verifying a slight increase in the frequency with the temperature.

## 5) Nematic Compound HPE

Figure 14 shows the dielectric anisotropy in the nematic phase of the compound HPE with a weak negative anisotropy; the transverse componente of the electric dipole moment is greater than the parallel component. The Figure 15 shows the variation with frequency of the dielectric constants ($\varepsilon'_{\perp}$) and the dielectric absorption ($\varepsilon''_{\perp}$) at different temperatures. The relaxation frequency is localized at $1.5.10^6$ Hz.

Figure 16 shows the dielectric anisotropy of the three nematic compounds as a function of reduced temperatures. The anisotropy is greater in the compound CB5, because this biphenyl compound with a Cyanic group

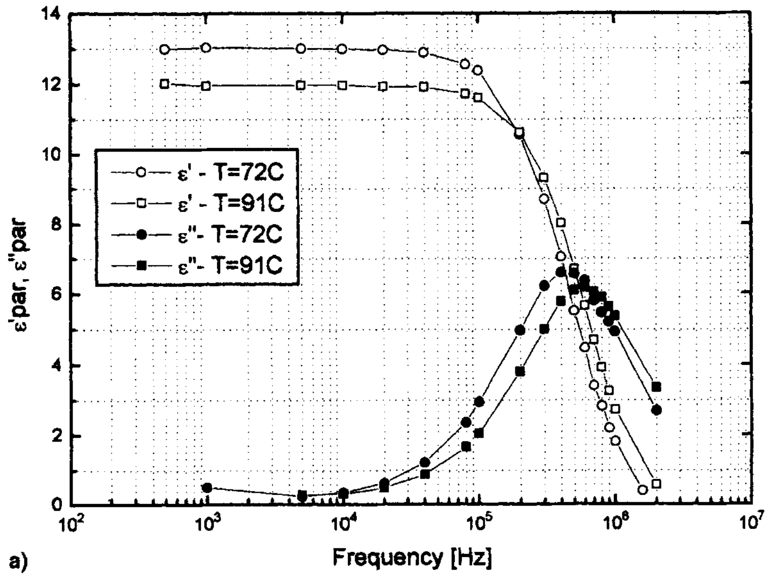


FIGURE 13a Frequency dependence of the dielectric constant ε'par and dielectric loss ε"par at different temperatures of the compound CBO-BCOAGCF.

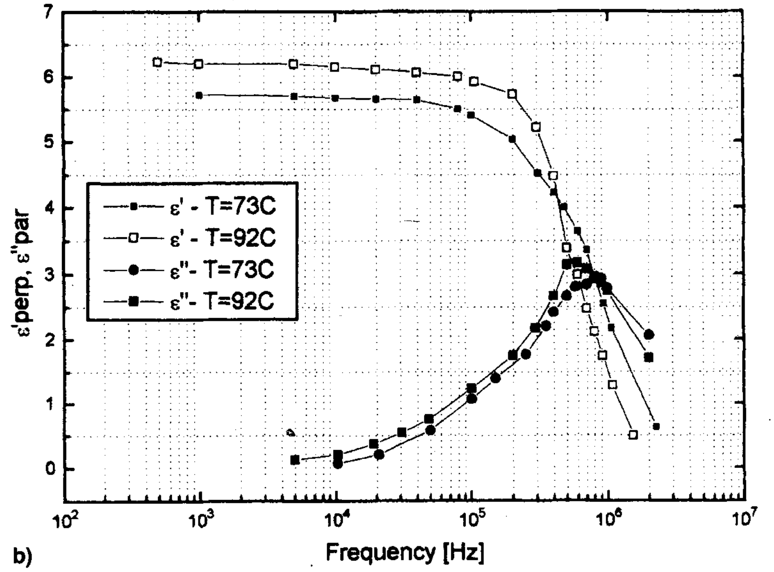


FIGURE 13b Frequency dependence of the dielectric constant ε'perp and dielectric loss ε"perp at different temperature of the compound BCO-BCOEGCF.

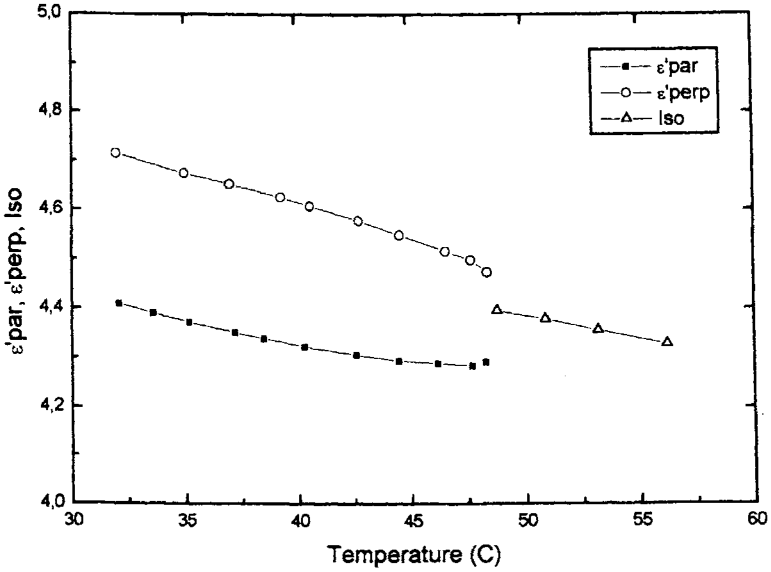


FIGURE 14 Dielectric anisotropy as a function of temperature of the compound HPE at $f = 7$ kHz-HPEAN.

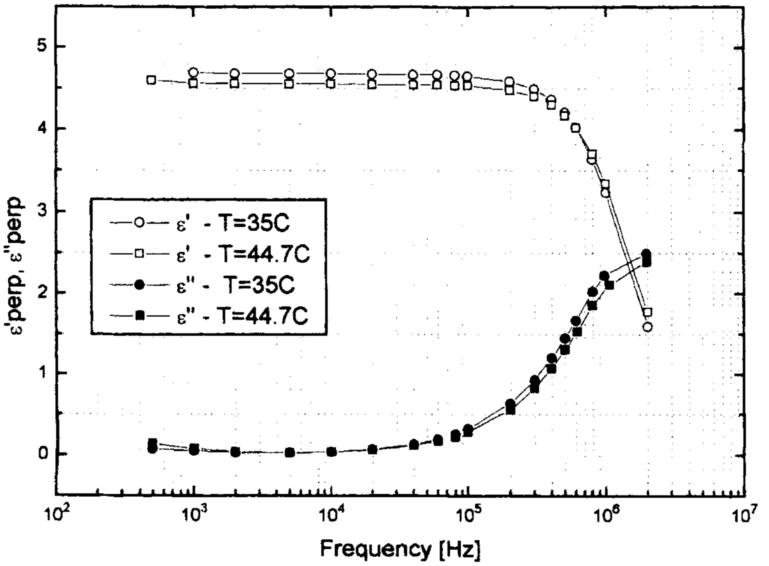


FIGURE 15 Frequency dependence of the dielectric constant ε'perp and dielectric loss ε"perp at different temperatures of the compound HPE-HPECG.

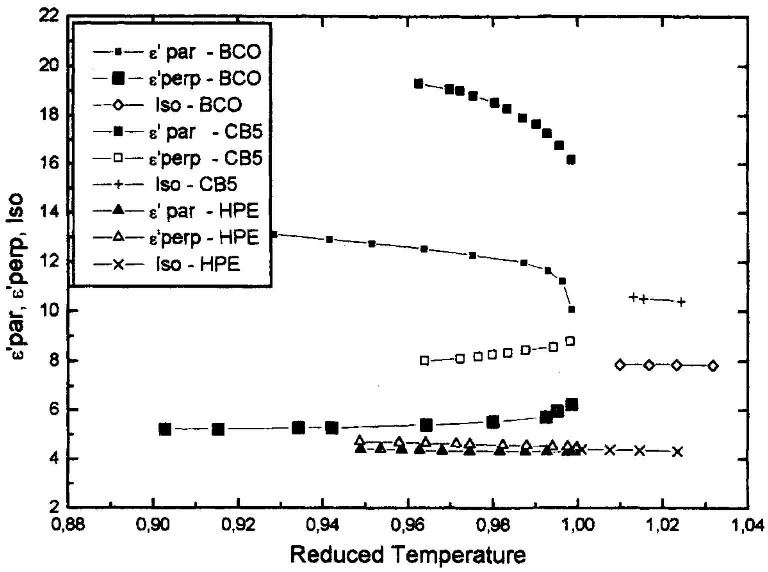


FIGURE 16 Dielectric anisotropy as a function of reduced temperature of the compounds CB5, BCO and HPE-ANISOTRO.

has a very strong electric dipole moment in the longitudinal direction and this compound is already known [13] and was taken more for comparison with the others. The compound BCO still has a positive anisotropy, but smaller compared to CB5. The compound HPE has a negative anisotropy, due to the ester group and the magnitude is very small. We note that the relaxation frequency increases in the sequence CB5 (3.10$^5$ Hz), BCO (4.5.10$^5$ Hz) and HPE (1.5.10$^6$ Hz).

## *Acknowledgement*

This work was supported by the Universidade Federal de Santa Catarina and by CNP$_q$.

## *References*

[1] R. B. Meyer, Presentation at the 5th International Liquid Crystal Conference, Stockholem, 1974.
[2] R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. de Phys. Lett.*, **36**, L69 (1975).
[3] N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
[4] W. J. A. M. Hartmann, *Ferroelectrics*, **122**, 1 (1991).

[5] P. Maltese, *Molec. Cryst. Liq. Cryst.*, **215**, 57 (1992).
[6] B. Zeks, A. Levstik and R. Blinc, *J. Phys. (Paris) Colloq*, **40**, C3-409 (1979).
[7] R. J. Cava, J. S. Patel, K. R. Collen, J. W. Goodby and E. A. Rietman, *Phys. Rev.*, **A35**, 4378 (1987).
[8] A. Levstik, T. Carlsson, C. Filipic, I. Levsktik and B. Zeks, *Phys. Rev.*, **A35**, 3527 (1987).
[9] T. Pal Majumder, M. Mitra and S. K. Roy, *Phys. Rev.*, **E50**, 4796 (1994).
[10] R. E. Michel and G. W. Smith, *J. Appl.*, **45**, 3234 (1974).
[11] M. Schadt and F. Müller, *J. Phys.*, **14**, 265 (1982).
[12] M. Schadt and P. R. Gerber, *Z. Naturforsch.*, **37a**, 165 (1982).
[13] F. Gouda, E. Anderson, M. Matuszizyk, T. Matuszczyk, K. Skarp and S. T. Lagerwall, *J. Appl. Phys.*, **67**(**1**), 180 1 January (1990).
[14] K. Skarp and M. A. Handschy, *Mol. Cryst. Liq. Cryst.*, **165**, 439 (1988).
[15] S. S. Bawa, A. M. Biradar and S. Chandra, *Ferroelectrics*, **76**, 69 (1987).
[16] G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals*, Leonard and Hill, Glasgow and London, 1984.
[17] M. F. Bone, D. Coates and A. B. Davey, *Mol. Cryst. Liq. Cryst.*, **102**, 331 (1984).
[18] K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
[19] B. R. Ratana and R. Schashidhar, *Pramana*, **6**(5), 178 (1976).
[20] A. J. Leadbetter, R. M. Richardson and C. N. Colling, *J. Phys.*, **36**, C137 (1975).