

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Alpha sub-phase in a new ferroelectric fluorinated compound

M. Marzec Corresponding author^a; A. Mikułko^a; S. Wróbel^a; R. Dałbrowski^b; M. Darius^c; W. Haase^c

^a Institute of Physics, Jagiellonian University, 30-059 Kraków, Poland ^b Military University of Technology, 00-908 Warszawa, Poland ^c Institute of Physical Chemistry, TU Darmstadt, D-64287, Germany

Online publication date: 19 May 2010

To cite this Article Marzec Corresponding author, M. , Mikułko, A. , Wróbel, S. , Dałbrowski, R. , Darius, M. and Haase, W.(2004) 'Alpha sub-phase in a new ferroelectric fluorinated compound', *Liquid Crystals*, 31: 2, 153 – 159

To link to this Article: DOI: 10.1080/02678290310001639599

URL: <http://dx.doi.org/10.1080/02678290310001639599>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Alpha sub-phase in a new ferroelectric fluorinated compound

M. MARZEC*, A. MIKUŁKO, S. WRÓBEL

Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków,
Poland

R. DĄBROWSKI

Military University of Technology, Kaliskiego 2, 00-908 Warszawa, Poland

M. DARIUS and W. HAASE

Institute of Physical Chemistry, TU Darmstadt, Petersenstr. 20, D-64287,
Germany

(Received 16 July 2003; accepted 30 September 2003)

Dielectric and DSC methods were used to study a new fluorinated liquid crystalline compound exhibiting ferroelectric and paraelectric phases as well as an intermediate alpha sub-phase. Two dielectric relaxation processes were revealed in the SmC^* phase: a typical Goldstone mode over the whole temperature range and a soft mode in the pre-transition region on both sides of the SmC^* – SmA^* transition. From the temperature dependencies of the dielectric increments and critical frequencies for the dielectric relaxation processes observed in all the liquid crystalline phases, as well as from texture observations, it was shown that there is a SmC^*_{α} sub-phase between the ferroelectric SmC^* and paraelectric SmA^* phases.

1. Introduction

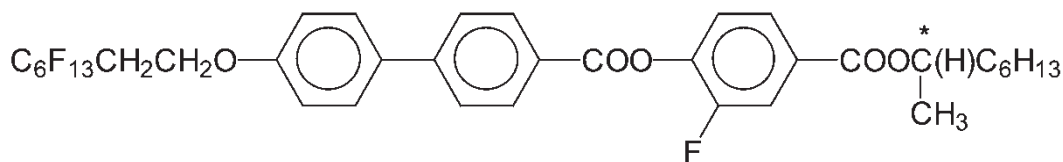
Ferroelectric liquid crystals (FLCs) have been extensively studied since their discovery in 1974 by Meyer *et al.* [1]. The temperature-dependent behaviour of the dielectric relaxation modes, the tilt angle and the spontaneous polarization in the vicinity of the ferro- and para-electric transitions have been theoretically described by Blinc and Žekš [2]. Since 1988 when antiferroelectric liquid crystals (AFLCs) were discovered, considerable experimental and theoretical work has been performed. In particular, it has been shown that between antiferro-, ferro- and para-electric phases, additional sub-phases appear in the phase diagrams of some materials, for example, the SmC^*_{γ} sub-phase between the antiferroelectric SmC^*_{A} and ferroelectric SmC^* phases; or the SmC^*_{α} sub-phase between the SmC^* and paraelectric SmA^* phases [3].

The structure of the SmC^*_{α} sub-phase is not yet well understood. It is described as a tilted ferroelectric like phase in its low temperature range, as an antiferroelectric phase in the high temperature range and as ferroelectric-like in the intermediate range [4, 5]. Several phenomenological models have been proposed to

describe the sub-phases, for example, the discrete model of Čepič and Žekš [6]. It was shown that the SmC^*_{α} sub-phase is ferroelectric-like with a very short pitch of the helix [7], and the phase angle difference between the directors in neighbouring layers can be between 0 and π [8]. Moreover, as the SmC^* , SmC^*_{A} and SmC^*_{α} phases seem to have the same point symmetry, one can then experimentally identify the SmC^*_{α} sub-phase only when the transition between the SmC^* and SmC^*_{α} phases is of the first order type [8]. To date some electro-optic and dielectric studies have been performed revealing the SmC^*_{α} phase [4–10]. It was shown that the alpha sub-phase in AFLCs exists only for optically pure compounds [11, 12] while mixtures containing other homologues (or their enantiomers) change the phase sequence from SmC^* – SmC^*_{α} – SmA^* to SmC^* – SmA^* .

The aim of this work is to present the results of DSC and dielectric studies performed on a new fluorinated liquid crystalline compound. The dielectric measurements and texture observations showed that in the phase diagram of this ferroelectric compound the SmC^*_{α} sub-phase exists between the ferroelectric SmC^* and paraelectric SmA^* phases.

*Author for correspondence; e-mail: ufmarzec@if.uj.edu.pl



Cr. – 83.4 °C – SmC* – 134.8 °C – SmA* – 155.6 °C – I

Figure 1. Molecular structure and phase behaviour of MHP(F)O(13F)BC.

2. Experimental

The molecular structure of the new compound is based on that of the MHPOBC series [13, 14]. The molecular structure and phase transitions of *S*-(+)-4-(1-methylheptyloxy carbonyl)-3-fluorophenyl 4-(1H, 1H, 2H, 2H perfluorooxy)biphenyl-4'-carboxylate, MHP(F)O(13F)BC, are shown in figure 1.

The thermal stability of the substance studied is very good; during the DSC studies many heating and cooling runs were performed and thermal parameters such as transition temperatures, enthalpies and entropies did not vary with time. The same behaviour was found during studies on this material under strong electric fields up to $12 \text{ V } \mu\text{m}^{-1}$. As far as purity is concerned, the substance displays enhanced electrical conductivity just below 100 Hz ($\sigma = 9.5 \times 10^{-9} \text{ S m}^{-1}$) which is reasonable for a fluorinated material.

A Perkin-Elmer PYRIS 1 DSC was used to study the thermal behaviour of the compound. Aluminium pans were used for these measurements, which were performed in the temperature range 20–170 °C. Heating and cooling rates were equal and varied between 5 and 80 K min^{-1} .

The dielectric measurements were performed by means of frequency domain dielectric spectroscopy (FDSD) using a HP 4192A impedance analyser. A gold-coated cell having a capillary gap of $23 \mu\text{m}$ was used. The sample was filled using the capillary effect in the isotropic phase, and then planar alignment was achieved by means of an electric field of $1.14 \text{ V } \mu\text{m}^{-1}$ applied upon slow cooling at the SmA*–SmC*_α–SmC* transition so as to obtain a mono-domain sample.

3. Results and discussion

3.1. DSC studies and microscopy observations

DSC heating and cooling runs obtained for MHP(F)O(13F)BC with a heating/cooling rate of 10 K min^{-1} are shown in figure 2. There are three anomalies in the DSC heating and cooling runs. The transition to the solid state during cooling is shifted towards lower temperatures as compared with the melting point seen on heating. Such behaviour is characteristic for substances exhibiting liquid crystalline phases. DSC measurements were performed for seven

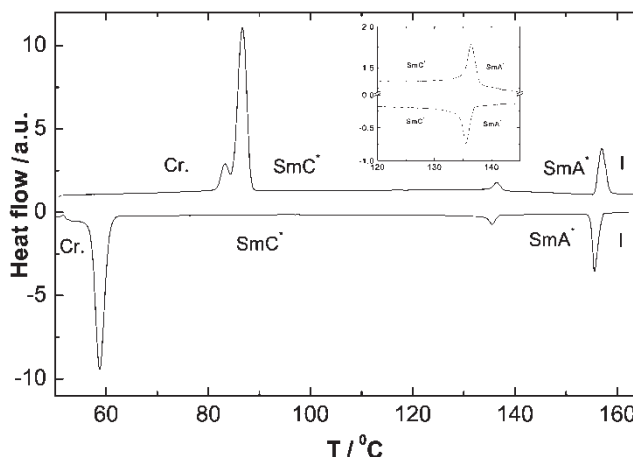


Figure 2. DSC curves obtained with heating and cooling rates of 10 K min^{-1} .

different heating and cooling rates: 5, 10, 20, 30, 40, 60, 80 K min^{-1} . The temperatures of the melting and clearing points, as well as the SmA*–SmC* transitions, for each rate are gathered in table 1. As can be seen, the temperature of the melting point changes with heating rate whereas the temperature of the clearing point seems to be rate-independent. Such dependencies represent common behaviour for liquid crystalline substances and indicate good thermal stability for the sample. The DSC studies made for different heating/cooling rates showed no qualitative changes in the thermograms. Thus the rate does not influence the phase behaviour of this compound.

Table 1. Onset temperatures of the melting and clearing points acquired for different heating rates.

Rate/ K min^{-1}	Melting point/°C	Clearing point/°C	SmA*– SmC*/°C
5	84,8	155,6	135,2
10	85,0	155,6	135,2
20	84,9	155,8	135,2
30	84,6	155,9	135,2
40	84,5	155,8	135,0
60	83,1	155,8	134,8
80	82,9	155,6	134,3

The nature of the particular phases was determined using polarizing optical microscopy. The different characteristic textures observed are shown in figure 3. Figure 3 (a) shows the texture of the crystal phase, while (b), (c), (d) are liquid crystalline textures. A slight difference between figures 3 (b) and 3 (c) may suggest that an additional sub-phase, for example, SmC*_α (c), exists between the ferroelectric SmC* (b) and paraelectric SmA* (d) phases. It is worth stressing here that on the DSC thermogram there was no anomaly associated with the transition between the SmC* and SmC*_α phases apparent in the texture observations. Lagerwall *et al.* [15] concluded that the sub-phases (SmC*_α, SmC*_β, SmC*_γ) could appear only in AFLCs but they also suggest that the SmC*_α sub-phase should be discussed separately. Here we assume that the SmC*_α sub-phase may also appear in FLCs. We now turn to dielectric studies to substantiate the existence of

the SmC*_α sub-phase for the ferroelectric compound studied.

3.2. Dielectric studies

The dielectric measurements were carried out as a function of temperature on a planar oriented sample. A bias voltage of 25 V was applied in the ferroelectric SmC* phase to suppress the Goldstone mode (GM) contribution and to study the soft mode (SM) evident close to the critical temperature. In the SmC* phase a typical GM with dielectric increment of *ca.* 326 was detected, and in the SmC*–SmA* pre-transition region the SM was also observed. For example, figure 4 shows the dielectric spectrum taken without a bias field at 131.4°C, i.e. in the pre-transition region just below T_c . One can see that the dielectric spectrum consists of two not well separated absorption peaks. The solid line in this figure is the fit using the sum of two Cole–Cole

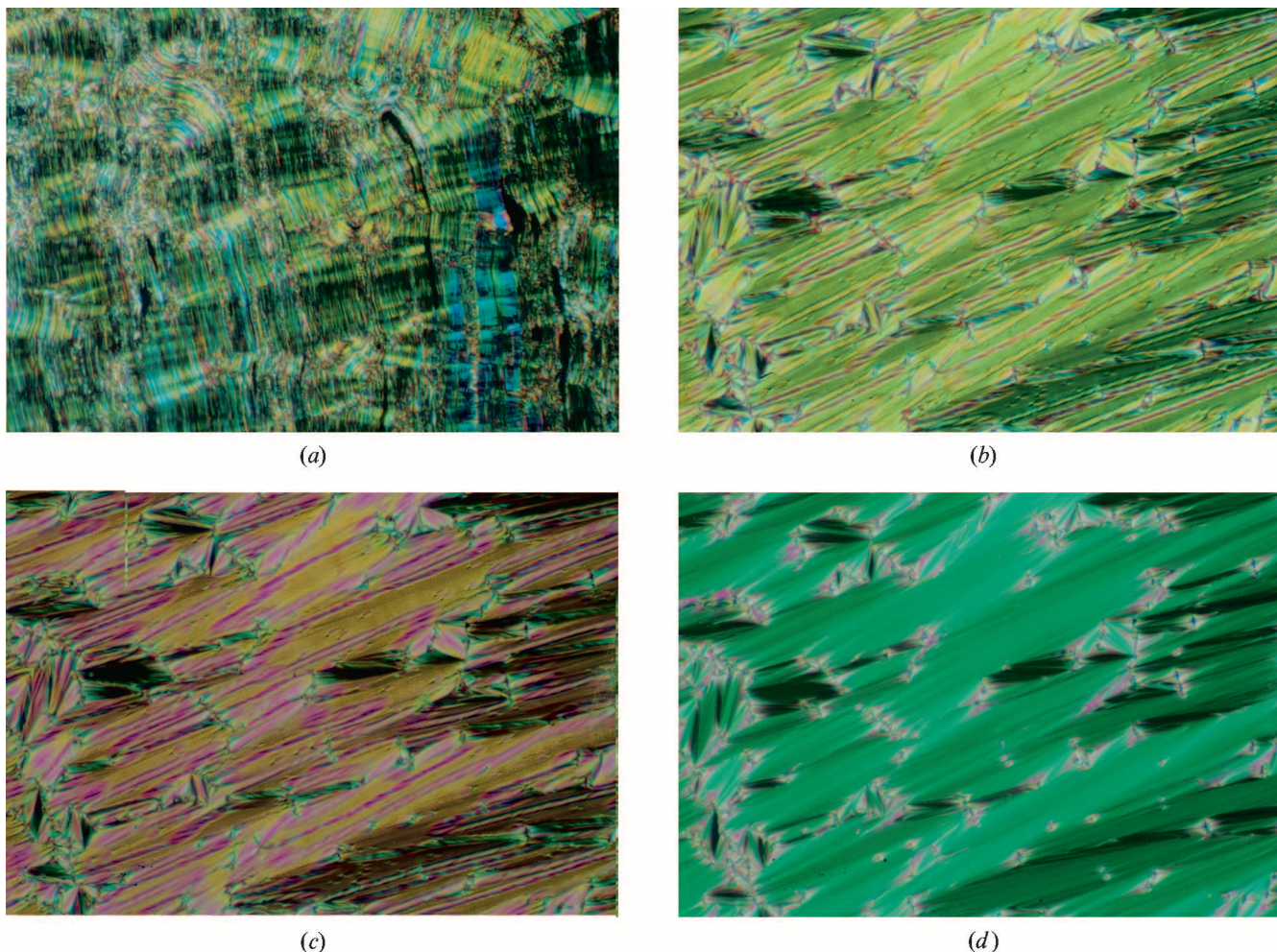


Figure 3. Textures of the crystal and liquid crystalline phases observed under, crossed polarizers, magnification 300, thickness of the cell 10 μm . (a) Crystal phase, 56°C; (b) SmC* phase, 120°C; (c) SmC*_α phase, 133.7°C; (d) SmA* phase, 150°C.

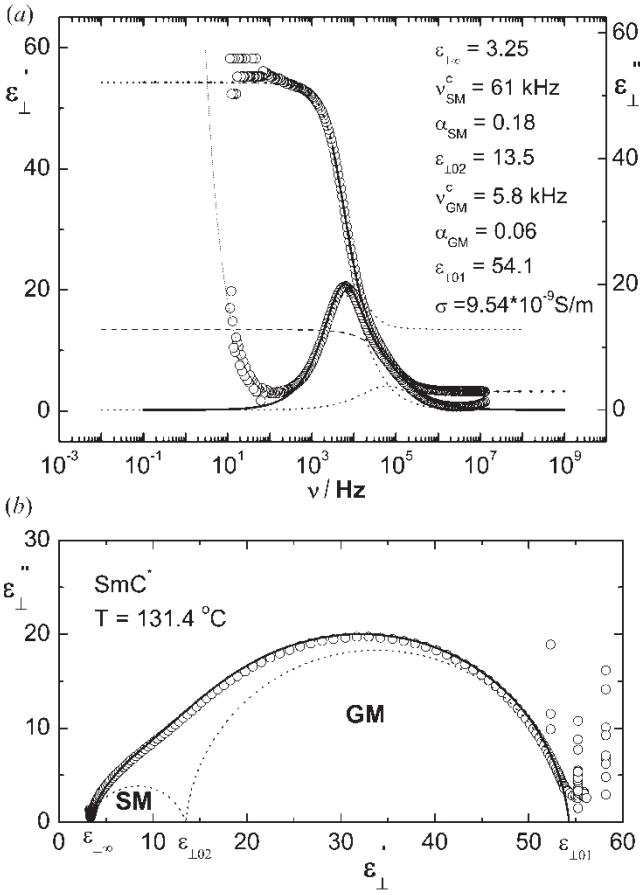


Figure 4. Absorption and dispersion curves (a) and Cole – Cole plot (b) in the pre-transition region.

functions including a conductivity contribution:

$$\begin{aligned} \varepsilon_{\perp}^* = \varepsilon'_{\perp} - i\varepsilon''_{\perp} = \varepsilon_{\perp\infty} + \frac{\Delta\varepsilon_{SM}}{1 + (i\omega\tau_{SM})^{1-\alpha_{SM}}} \\ + \frac{\Delta\varepsilon_{GM}}{1 + (i\omega\tau_{GM})^{1-\alpha_{GM}}} - i\frac{\sigma_{\perp}}{\varepsilon_0\omega} \end{aligned} \quad (1)$$

where $\Delta\varepsilon_{GM} = \varepsilon_{01} - \varepsilon_{02}$ is the GM contribution to the dielectric spectrum, and $\Delta\varepsilon_{SM} = \varepsilon_{02} - \varepsilon_{\perp\infty}$ is due to the soft mode dielectric relaxation process. ω is the angular frequency ($\omega = 2\pi\nu$), $\varepsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$ is the dielectric permittivity of free space, τ_{GM} and τ_{SM} are the dielectric relaxation times for the Goldstone and soft mode, respectively, $\varepsilon_{\perp\infty}$ is the high frequency limit of the dielectric permittivity and σ is the ionic conductivity of the substance studied. Dashed lines are the contributions of the two collective modes, obtained during the fitting procedure. The soft mode was seen clearly in the SmC* phase using a gold-coated cell under a bias field of 25 V/23 μm which completely suppressed the GM contribution to the dielectric spectrum. One can see in figure 5 how the bias voltage influences the dielectric spectrum in the pre-transition

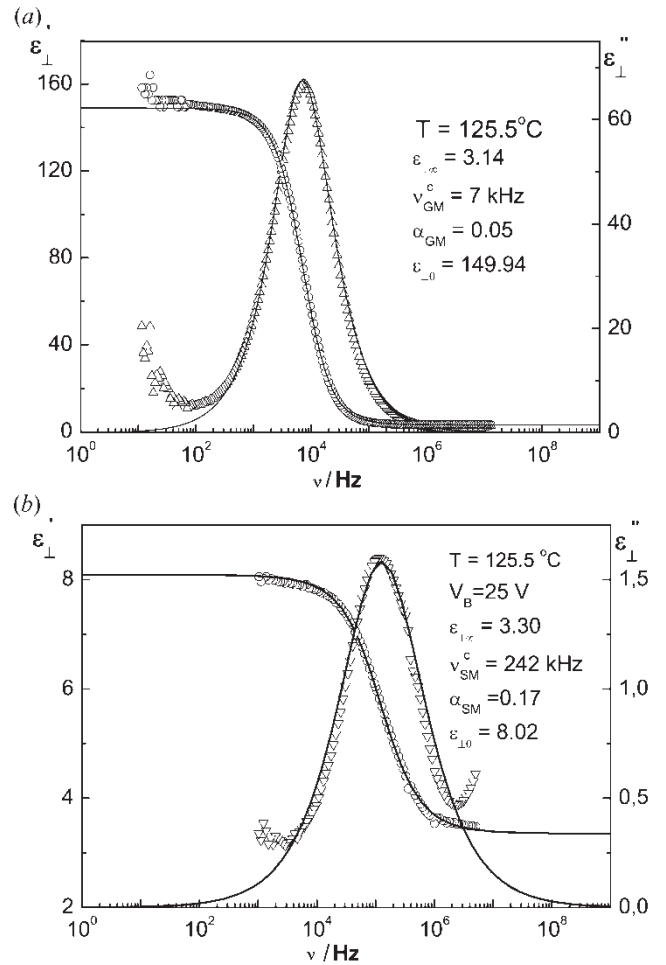


Figure 5. Influence of the bias field on the dielectric spectrum: (a) $V_B = 0\text{V}$, GM; (b) $V_B = 25\text{V}$, SM.

region. Figure 5(a) shows an intensive GM covering the SM while in figure 5(b) only the SM under a bias voltage of 25 V is observed.

The temperature dependencies of the dielectric increments and of the critical frequencies for the Goldstone and soft modes are shown in figure 6. The slopes of the straight lines fitted to these dependencies for the SM on both sides of the para-ferroelectric phase transition and the ratio of the slopes are gathered in table 2.

One can see that the slopes of $\Delta\varepsilon_{SM}^{-1}$ and $\nu_{SM}^c(T)$ calculated from the experimental data in the SmC* phase are much smaller than those in the SmA* phase, and the ratios of the slopes are very different from the value of -2 predicted by Blinc-Žekš theory for a second order transition [2]. Therefore one can conclude that we are not dealing here with a simple SmA*–SmC* second order transition. One can suggest, as with the discussion of the textures, that an additional sub-phase exists between the ferroelectric and paraelectric phases. Furthermore a careful analysis of the temperature

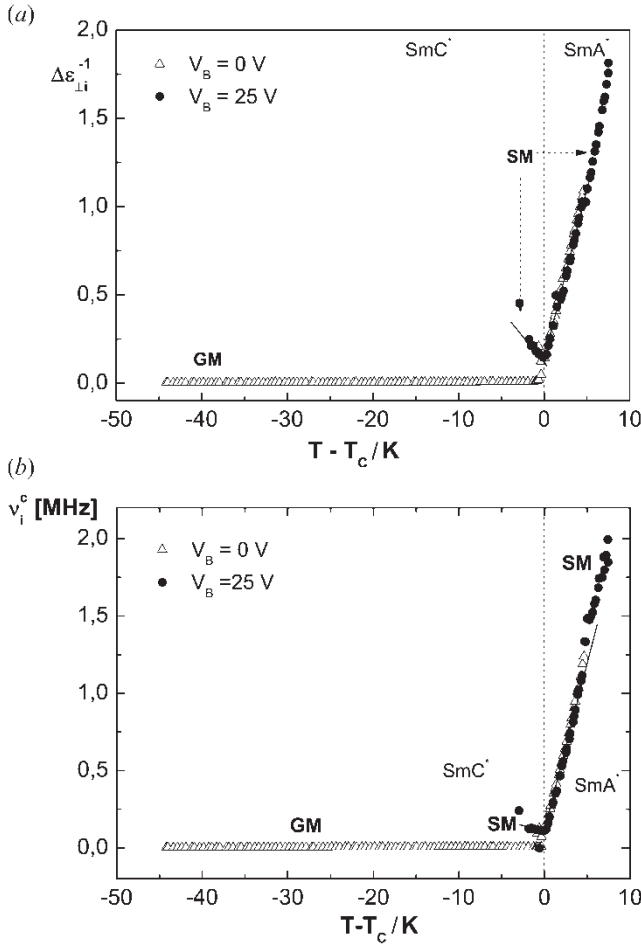


Figure 6. Temperature dependencies of (a) the dielectric increments and (b) critical frequencies for the Goldstone and soft modes in the ferroelectric and paraelectric phases.

dependencies of the dielectric increment and of the critical frequency in the pretransition region for the processes observed in the ferro- as well as in the paraelectric phase (see figure 7) reveals two anomalies in the temperature dependencies of $\nu_1^c(T)$ (a) and $\Delta\epsilon_{\perp}(T)$, $\Delta\epsilon_{\perp}^{-1}(T)$ (b): one at T_c and the second one at about $T_c - 2$ K. The anomalies are clearly seen on the $\Delta\epsilon_{\perp}(T)$ curve as slope changes. Such anomalies were observed previously [9, 10] and indicate that the SmC^*_{α} phase exists in the intermediate temperature range.

Table 2. The slopes of the soft mode dielectric parameters and their ratios in the vicinity of the SmA^* - SmC^* phase transition.

Slope	$\frac{d}{dT} \Delta\epsilon_{SM}^{-1}(T)$	$\frac{d}{dT} \nu_{SM}^c(T)$
SmC*	$E_1 = -0,047 \pm 0,004$	$N_1 = -12,4 \pm 0,5$
SmA*	$E_2 = 0,20 \pm 0,02$	$N_2 = 211,5 \pm 6,9$
Ratio of the slopes	$E_1/E_2 = -0,24 \pm 0,04$	$N_1/N_2 = -0,06 \pm 0,01$

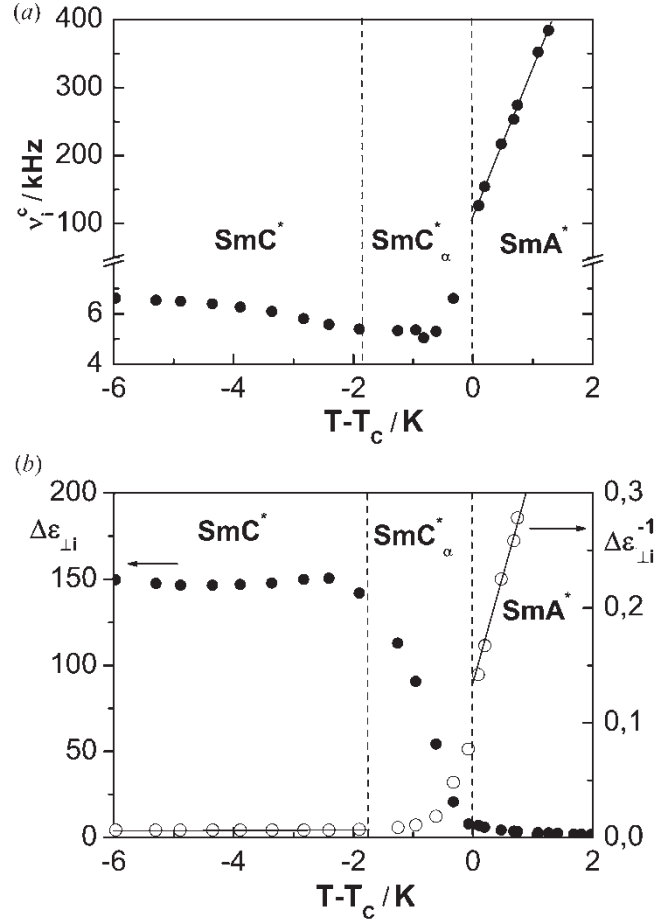


Figure 7. Temperature dependencies of (a) ν_1^c and (b) $\Delta\epsilon_{\perp}^{-1}$ in the vicinity of T_c .

These anomalies can also be observed at different frequencies, as seen in figure 8. This confirms the existence of the additional sub-phase.

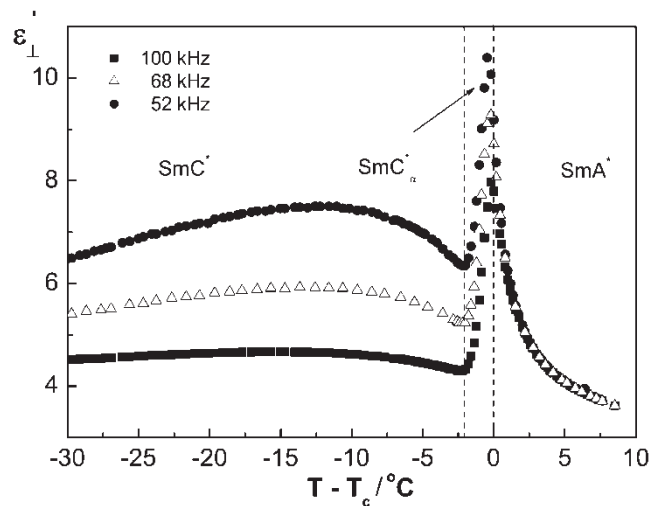


Figure 8. Temperature dependence of the dielectric permittivity.

It appears, therefore, that the alpha sub-phase exists for the new substance as well as for other optically pure compounds [11, 12], even though Górecka *et al.* [16] showed that for MHPBC the SmC^*_α sub-phase disappears when the enantiomeric excess is less than 0.5. In view of this, the lowest temperature liquid crystalline phase may not be a regular ferroelectric SmC^* phase but a ferroelectric SmC^*_β sub-phase, as has been shown for other compounds by Tatemori *et al.* [12], Sako *et al.* [17] and Uehara *et al.* [18]. Recently, Górecka *et al.* [16, 19] and Lagerwall *et al.* [15] have shown that the SmC^*_β sub-phase is not ferroelectric but antiferroelectric. The SmC^* phase could appear between the SmC^*_α and SmC^*_β sub-phases or instead of the SmC^*_β phase; this depends on the purity resulting from temperature-induced chemical degradation [15]. Yet in our case the substance under investigation seems to be a ferroelectric liquid crystal. Therefore to study whether the SmC^*_β sub-phase is present for MHP(F)O(13F)BC, the dielectric permittivity, measured at 1 kHz as a function of the bias field, was plotted for three different temperatures in the SmC^* phase, far from the transition to paraelectric phase (see figure 9). As one can see, the decrease in ϵ'_\perp as a function of bias field is a single step, which is characteristic of a ferroelectric SmC^* phase [12, 18]. Thus this is evidence that the alpha sub-phase exists between ferroelectric SmC^* and paraelectric SmA^* phases in FLCs. Hence, based on the results of the dielectric studies the following new phase sequence of MHP(F)O(13F)BC is proposed: $\text{Cr}-89.7^\circ\text{C}-\text{SmC}^*-133.0^\circ\text{C}-\text{SmC}^*_\alpha-134.8^\circ\text{C}-\text{SmA}^*-154.7^\circ\text{C}-\text{I}$.

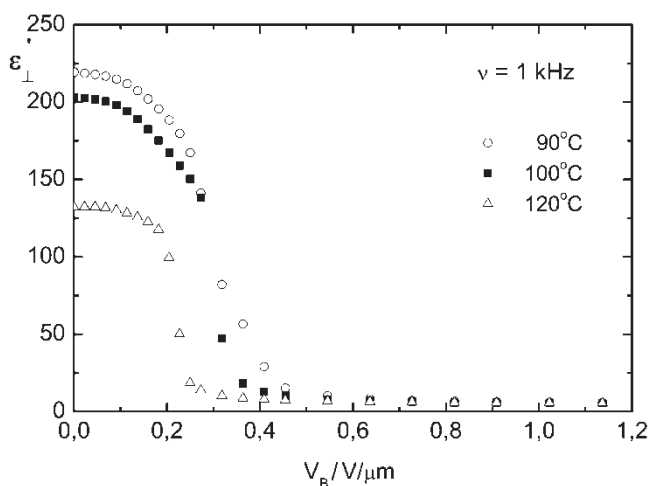


Figure 9. Bias field dependence of dielectric permittivity in the SmC^* phase for three temperatures.

4. Conclusions

DSC measurements show that two liquid crystalline phases are seen on heating and cooling MHP(F)O(13F)BC, while dielectric measurements and microscopy observations indicate three liquid crystalline phases: ferroelectric, paraelectric and an alpha sub-phase (SmC^*_α). The dielectric studies show a characteristic Goldstone mode in the ferroelectric SmC^* phase. On both sides of the transition temperature T_c between the ferro- and para-electric phases the characteristic soft mode was detected in the dielectric spectrum. From the temperature dependencies of the dielectric increment, critical frequency and dielectric permittivity, an additional intermediate SmC^*_α sub-phase between the ferroelectric and paraelectric phases has been demonstrated. The possibility of an antiferroelectric SmC^*_β sub-phase in the phase sequence of this substance was excluded. Further measurements of spontaneous polarization and tilt angle should be made to confirm this conclusion and to describe the order of the $\text{SmC}^*-\text{SmC}^*_\alpha-\text{SmA}^*$ transitions.

References

- [1] MEYER, R. B., LIEBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys. Fr.*, **36**, L69.
- [2] BLINC, R., and ŽEKŠ, B., 1978, *Phys. Rev. A*, **18**, 740.
- [3] ISOZAKI, T., FUJIKAWA, T., TAKEZOE, H., FUKUDA, A., HAGIWARA, T., SUZUKI, Y., and KAWAMURA, I., 1993, *Phys. Rev. B*, **48**, 13439.
- [4] BAHR, CH., FLIEGNER, D., BOOTH, C. J., and GOODYBY, J. W., 1995, *Phys. Rev. E*, **51**, R3823.
- [5] LAUX, V., ISAERT, N., JOLY, G., and NGUYEN, H. T., 1999, *Liq. Cryst.*, **26**, 361.
- [6] ČEPIČ, M., and ŽEKŠ, B., 1995, *Mol. Cryst. liq. Cryst.*, **263**, 61.
- [7] ORTEGA, J., FOLCIA, C. L., ETXEBARNIA, J., and ROS, M. B., 2003, *Liq. Cryst.*, **30**, 109.
- [8] ŠKARABOT, M., ČEPIČ, M., ŽEKŠ, B., BLINC, R., HEPPKE, G., KITIK, A. V., and MUŠEVIČ, I., 1998, *Phys. Rev. E*, **58**, 575.
- [9] DOUALI, R., LEGRAND, C., FAYE, V., and NGUYEN, H. T., 1999, *Mol. Cryst. liq. Cryst.*, **328**, 209.
- [10] DOUALI, R., LEGRAND, C., and NGUYEN, H. T., 2000, *Ferroelectrics*, **245**, 101.
- [11] TATEMORI, S., UEHARA, H., SAITO, S., SAITO, H., and OKABE, E., 2000, *Ferroelectrics*, **244**, 241.
- [12] TATEMORI, S., UEHARA, H., HATANO, J., SAITO, H., SAITO, S., and OKABE, E., 1999, *Jpn. J. appl. Phys.*, **38**, 5657.
- [13] CHANDANI, A. D. L., HAGIWARA, T., SUZUKI, Y., OUCHI, Y., TAKEZOE, H., and FUKUDA, A., 1988, *Jpn. J. appl. Phys.*, **27**, L729.
- [14] CHANDANI, A. D. L., GÓRECKA, E., OUCHI, Y., TAKEZOE, H., and FUKUDA, A., 1989, *Jpn. J. appl. Phys.*, **28**, L1265.
- [15] LAGERWALL, J. P. F., RUDQUIST, P., LAGERWALL, S. T., and GIEBELMANN, F., 2003, *Liq. Cryst.*, **30**, 399.

- [16] GÓRECKA, E., POCIECHA, D., ČEPIČ, M., ŽEKŠ, B., and DĄBROWSKI, R., 2002, *Phys. Rev. E*, **65**, 061 703.
- [17] SAKO, T., KIMURA, Y., HAYAKAWA, R., and OKABE, N., 1996, *Jpn. J. appl. Phys.*, **35**, L114.
- [18] UEHARA, H., IINO, Y., and HATANO, J., 1997, *Jpn. J. appl. Phys.*, **36**, 6118.
- [19] ČEPIČ, M., GÓRECKA, E., POCIECHA, D., and VAUPOTIČ, N., 2003, *Relaxation Phenomena. Liquid Crystals, Magnetic Systems, Polymers, High- T_c Superconductors, Metallic Glasses*, edited by W. Haase and S. Wróbel (Berlin-Heidelberg: Springer-Verlag), pp. 332–361.