

Characteristics of the collective dielectric relaxation mode of the incommensurate SmC_α^* phase

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 115207

(<http://iopscience.iop.org/0953-8984/20/11/115207>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 11:09

Please note that [terms and conditions apply](#).

Characteristics of the collective dielectric relaxation mode of the incommensurate SmC_α^* phase

M B Pandey^{1,4}, R Dhar² and R Dabrowski³

¹ Physics Department, University of Allahabad, Allahabad-211 002, India

² Physics Department, Ewing Christian College, Allahabad-211 003, India

³ Institute of Chemistry, Military University of Technology, 00-908, Warsaw, Poland

E-mail: mbpandey@gmail.com

Received 16 November 2007, in final form 24 January 2008

Published 20 February 2008

Online at stacks.iop.org/JPhysCM/20/115207

Abstract

Employing the dielectric relaxation spectroscopy technique, we have observed two different characteristics of the collective relaxation mode of an incommensurate SmC_α^* phase. Recent theoretical advances predict two different natures for the dielectric relaxation mode in the SmC_α^* phase. Our experimental results confirm two different behaviours of the relaxation mode in different temperature ranges for this phase for one unique compound having an exceptionally wide temperature range ($\sim 9^\circ\text{C}$) for the SmC_α^* phase.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The SmC_α^* phase is one of the subphases exhibited by antiferroelectric liquid crystal materials below the paraelectric SmA^* phase [1]. The structure of the SmC_α^* phase has been determined to be a uniaxial and incommensurate nanoscale helical pitch extending from three to eight smectic layers [2, 3]. The molecules within each layer are oriented with their long axes along a common direction represented by a tilt angle (θ) relative to the layer normal and an azimuthal angle (α). Due to the molecular chiralities, α changes from layer to layer and precesses about the smectic layer normal forming a helical structure. The optical period and, hence, the azimuthal angle difference ($\Delta\alpha$) between two smectic layers in this phase are found to vary with temperature. Due to change in the value of $\Delta\alpha$, the SmC_α^* phase shows properties similar to those of the antiferroelectric phase in the vicinity of the $\text{SmA}^*-\text{SmC}_\alpha^*$ transition and ferroelectric like properties on approaching the $\text{SmC}_\alpha^*-\text{SmC}^*$ transition. In the dielectric spectrum of the SmC_α^* phase, generally a single collective relaxation mode is observed for a planar oriented sample that exists in the high kHz region [4–8]. The origin of this mode is assigned as tilt fluctuation of molecules, i.e. it is a soft mode. In a few

materials this mode has been observed in the low kHz region and its origin has been assigned as a Goldstone mode [9]. A theoretical model has been proposed by Vaupotic *et al* to explain the dielectric relaxation mechanism of SmC_α^* and other chiral tilted smectic phases [10]. They have predicted the existence of two dielectric relaxation processes, namely amplitude and phase fluctuation modes, in the SmC_α^* phase. Recently we have observed two dielectric modes in the SmC_α^* phase of a chlorinated MHPOBC compound [11]. We have demonstrated temperature and bias electric field dependence of two relaxation modes of the SmC_α^* phase, concurring with the theoretical work of Vaupotic *et al*. The theory of Vaupotic *et al* has been further extended by Douali *et al* for the SmC_α^* phase by taking different values of model coefficients of the free energy equation. This work is supported by their optical and dielectric experiments [12]. They have found that the temperature dependence of the experimentally observed dielectric mode of SmC_α^* phase could only be explained by considering the existence of two modes, as predicted by theory. However, this theory has not been convincingly verified for a general system having a wide temperature range of the SmC_α^* phase. So far, dielectric measurements of the SmC_α^* phase have turned out to be quite difficult, because this phase generally exists in very narrow temperature range ($\sim 1^\circ\text{C}$) along with several other chiral smectic subphases. Hence dielectric data

⁴ Author to whom any correspondence should be addressed.

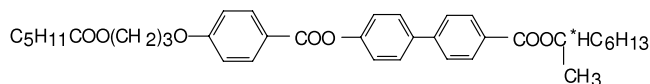


Figure 1. The molecular structure of the compound investigated (S)-(+)-4-(1-methylheptyl) 4-[(4-(3-hexanoyloxy) prop-1-oxy) benzoyloxy] biphenylate.

for the SmC_{α}^* phase are generally affected due to the adjacent low temperature phase which increases the ambiguity of results and their interpretation.

In this work we are reporting the dielectric investigation of a relaxation mode of a compound (S)-(+)-4-(1-methylheptyl) 4-[(4-(3-hexanoyloxy) prop-1-oxy) benzoyloxy] biphenylate (see figure 1) that shows an exceptionally wide temperature range of the SmC_{α}^* phase ($\sim 9^{\circ}C$). This compound possesses only SmC_{α}^* and SmA^* phases between crystal and isotropic liquid phases. Our results unambiguously prove two different behaviours of the relaxation mode in the SmC_{α}^* phase and lend strong support to the proposed dielectric theory [10, 12].

2. Experimental details

The phase transition temperatures have been determined by using a differential scanning calorimeter (DSC) from Perkin-Elmer and a transmitted light polarizing microscope. The dielectric measurements have been carried out with the help of an impedance/gain phase analyser from Solartron (model SI-1260) coupled with a Solartron dielectric interface (model-1296) in the frequency range of 1 Hz to 10 MHz. The dielectric cell was made from indium tin oxide (ITO) coated glass electrodes whose surfaces were chemically treated for planar orientation. Samples of two thicknesses were studied by using Mylar spacers of thicknesses 5 and 10 μm between two glass electrodes. A measuring ac voltage of 0.1 V_{rms} was applied across the sample in the direction parallel to the smectic layers. The temperature of the sample was controlled with the help of a hot stage from Instec (model HS-1) having the accuracy of $\pm 0.1^{\circ}C$. The actual temperature near the sample was determined by measuring the thermo-emf of a copper-constantan thermocouple with the help of a six-and-half-digit multimeter with the accuracy of $\pm 0.1^{\circ}C$. The other details of cell preparation and dielectric measurements are described elsewhere [13, 14].

To analyse the measured data, the dielectric spectra were fitted with the help of the generalized Cole-Cole equation [15, 16]

$$\begin{aligned} \varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) = \varepsilon'(\infty) + \frac{\Delta\varepsilon}{1 + (j\omega\tau)^{(1-h)}} + \frac{A}{\omega^n} \\ + \frac{\sigma(dc)}{j\varepsilon_0\omega} - jB\omega^m \end{aligned} \quad (1)$$

where $\varepsilon'(\infty)$ is the high frequency limiting value of the relative permittivity, $\Delta\varepsilon$, τ and h are the dielectric strength, the relaxation time (the inverse of the angular relaxation frequency) and the symmetric distribution parameter ($0 \leq h \leq 1$) of the relaxation mode respectively. The third and fourth terms in equation (1) are added due to the presence

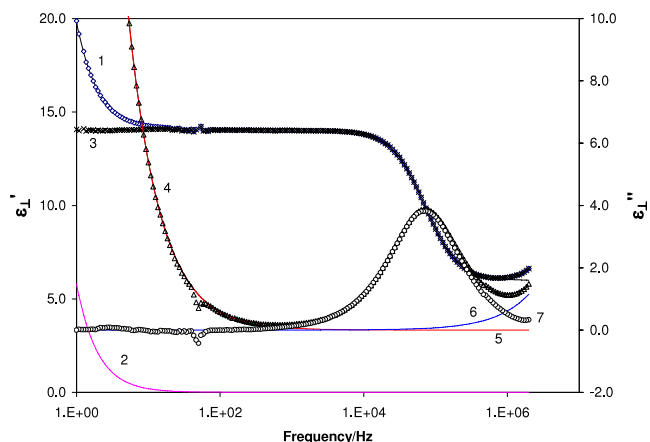


Figure 2. An example of mode analysis by simulation of experimental data using equation (1) for the SmC_{α}^* phase at $72.3^{\circ}C$.

of electrode polarization capacitance and ionic conductance at low frequencies, where A and n are fitting constants [8, 17]. $\sigma(dc)$ is the ionic conductance and ε_0 ($=8.85 \text{ pF m}^{-1}$) is the free space permittivity. The fifth imaginary term $B\omega^m$ [8, 17] is added in equation (1) to partially account for the ITO resistance and lead inductance, where B and m are constants as long as the correction terms are small. An example of a mode analysis of the relaxation process from low and high frequency artefacts for the simulation of experimental data with the help of equation (1) is shown in figure 2. In figure 2, curves (1)–(3) show the frequency dependence of the dielectric permittivity (ε'_1), the low frequency correction (LFC_P) due to the electrode polarization and corrected data for the dielectric permittivity after subtracting LFC_P from the measured data, respectively. Curves (4)–(7) show the measured dielectric loss (ε''_1), the low frequency correction (LFC_L) due to ionic conductivity, the high frequency correction (HFC_L) due to the ITO effect and corrected data for the dielectric loss after subtracting LFC_L and HFC_L from the measured ε''_1 respectively. The solid lines with curves (1) and (4) represent fitted curves which are in good agreement with experimental data.

3. Results and discussion

DSC thermograms for the heating and cooling cycles of the samples investigated are shown in figure 3. The phase sequence and transition temperatures as obtained from DSC at the scanning rate of $2.5^{\circ}C \text{ min}^{-1}$ are as follows.

Heating: Cr1 ($63.8^{\circ}C$) Cr2 ($70.5^{\circ}C$) SmC_{α}^* ($74.0^{\circ}C$) SmA^* ($100.0^{\circ}C$) Iso.

Cooling: Iso ($98.8^{\circ}C$) SmA^* ($75.4^{\circ}C$) SmC_{α}^* ($53.2^{\circ}C$) Cr2 ($50.1^{\circ}C$) Cr1.

The above mentioned phase sequences are also confirmed by optical textures and miscibility studies. It is important to mention that during the cooling cycle a SmC_{α}^* -Cr2 transition temperature as obtained by optical texture study has been observed at higher temperature than that observed from DSC. This is because during thermal scanning in DSC, the temperature variation is dynamic. Although the SmC_{α}^* -Cr2 transition starts at $\sim 63.8^{\circ}C$, being a dynamic process, the

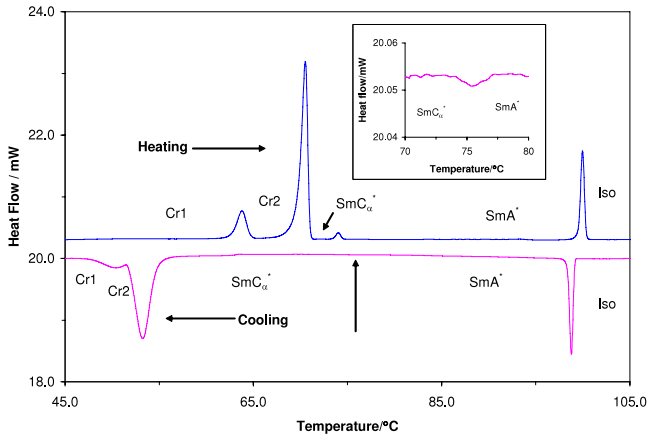


Figure 3. DSC thermogram for the scanning rate of $2.5\text{ }^\circ\text{C min}^{-1}$ in the heating and cooling cycles.

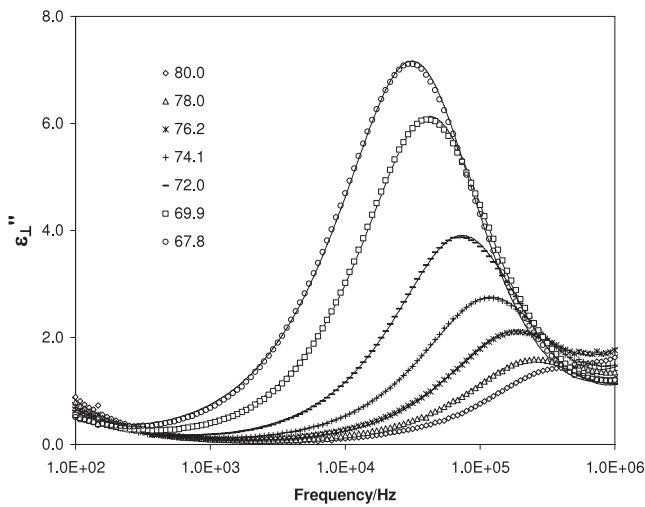


Figure 4. Dielectric absorption spectra at different temperatures for the SmA^* and SmC_α^* phases. The solid lines with experimental data represent the fitting of equation (1). Data below 100 Hz and above 1 MHz are highly affected due to low and high frequency effects and hence are not shown here, in order to enhance the visualization of the observed relaxation mode.

transition process has a DSC peak observed at $53.2\text{ }^\circ\text{C}$. During the optical texture study, the temperature variation is quasi-static. Once we see that a transition is taking place, we halt at that temperature ($64.8\text{ }^\circ\text{C}$) until the completion of the transition occurs.

The measured dielectric absorption spectra at various temperatures for SmA^* and SmC_α^* phases are shown in figure 4. The solid lines with measured curves present fittings of equation (1). The measured dielectric spectra of SmA^* and SmC_α^* phases are well described by single Debye and Cole-Cole type behaviours respectively. The dielectric strength ($\Delta\epsilon$), relaxation frequency (f_R) and distribution parameter (h) of the relaxation modes observed for the SmA^* and SmC_α^* phases are shown in figures 5–7 respectively. For the SmA^* phase, $\Delta\epsilon$ increases whereas f_R decreases continuously with decrease of temperature. The distribution parameters (h) have been found to be ~ 0 throughout the SmA^* phase. Taking

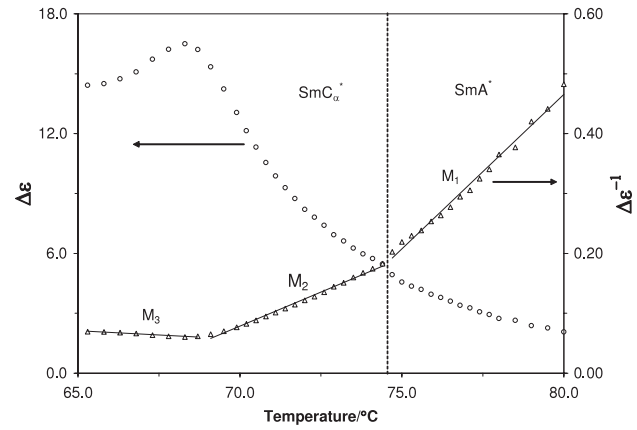


Figure 5. Temperature dependence of the dielectric strength ($\Delta\epsilon$) and the inverse of the dielectric strength ($\Delta\epsilon^{-1}$) in the cooling cycle of SmA^* and SmC_α^* phases for sample thickness $10\text{ }\mu\text{m}$. Vertical lines show the separation of two phases on the basis of dielectric parameters.

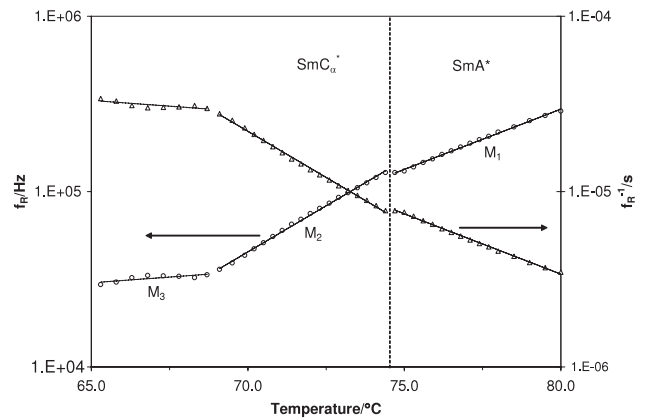


Figure 6. Temperature dependence of the relaxation frequencies (f_R) and inverse relaxation frequencies (f_R^{-1}) in the cooling cycle of SmA^* and SmC_α^* phases for sample thickness $10\text{ }\mu\text{m}$.

into account the molecular structure of the SmA^* phase and the temperature dependence of the dielectric parameters, this mode (M_1) must correspond to an amplitude mode (a so-called soft mode) which is associated with director tilt fluctuation of molecules in the smectic layers [8, 16].

On passing through the SmA^* – SmC_α^* transition, clear changes in the slopes of f_R and $\Delta\epsilon^{-1}$ have been observed (see figures 5 and 6). A sharp increase in the value of h has also been found at the SmA^* – SmC_α^* transition (see figure 7). The high value of h for the SmC_α^* phase (i.e. broadening of the relaxation peak) as compared to the orthogonal SmA^* phase may be assigned to the tilting of molecules in the SmC_α^* phase. On lowering the temperature of the sample in the SmC_α^* phase, f_R for this mode (M_2) decreases moderately and $\Delta\epsilon$ increases sharply with decrease in temperature to $69.0\text{ }^\circ\text{C}$ (see figures 5 and 6). The distribution parameter (h) remains constant (~ 0.06) between 74.4 and $69.0\text{ }^\circ\text{C}$. Below $69.0\text{ }^\circ\text{C}$, for the SmC_α^* phase, f_R becomes approximately invariant with temperature but $\Delta\epsilon$ decreases slowly with decrease in temperature. However, the value of h increases up to ~ 0.12

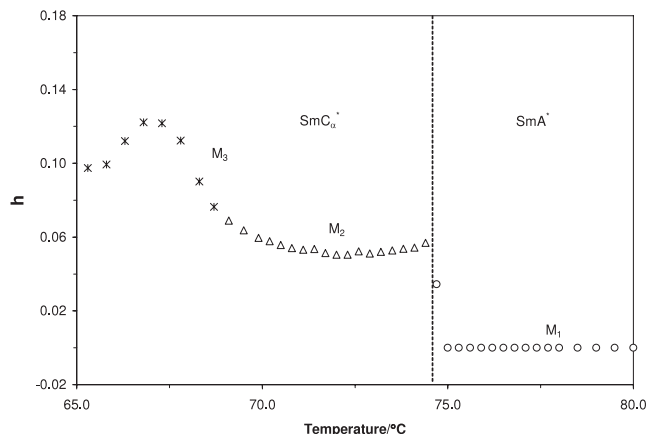


Figure 7. Temperature dependence of the distribution parameter (h) in the cooling cycle of SmA^* and SmC_α^* phases for sample thickness $10 \mu\text{m}$.

while going from 69.0 to 66.8°C . This clearly indicates that the behaviour of the observed mode (M_3) below 69.0°C is different as compared to those of M_2 . According to the theory of Vaupotic *et al*, two dielectric relaxation processes, namely amplitude and phase fluctuation modes, should be observed in the dielectric spectrum of the SmC_α^* phase [10]. In general, a single relaxation mode is reported for the SmC_α^* phase [4–8]. Its relaxation frequency varies in a fashion similar to that for the soft mode of the SmA^* phase but the slopes for the variation have been found to be different in the two cases [8]. To describe the behaviour of the experimentally observed relaxation mode in the SmC_α^* phase, theory proposed by Vaupotic *et al* has been extended by Douali *et al* [12]. On the basis of their simulation results, they have shown that the behaviour of the relaxation mode in the SmC_α^* phase depends upon the value of the azimuthal angle difference ($\Delta\alpha$) between the two smectic layers. A soft mode will be observed for high values of $\Delta\alpha > 100^\circ$ and the phase fluctuation mode will be dominant for low values of $\Delta\alpha < 25^\circ$ for the SmC_α^* phase. For intermediate values of $\Delta\alpha$ both types of relaxation mechanism could be observed. They have measured helical pitch in the SmC_α^* phase and then calculated values of $\Delta\alpha$. It has been found that $\Delta\alpha$ shows a maximum just below the $\text{SmA}^*-\text{SmC}_\alpha^*$ transition and thereafter it decreases with decrease in temperature. Hence the soft mode contribution is expected to be predominant in the vicinity of the $\text{SmA}^*-\text{SmC}_\alpha^*$ transition. However, far from the transition region, as the value of $\Delta\alpha$ decreases, a phase fluctuation mode should be observed.

In the present study, it has been found that the relaxation frequency (f_R) and dielectric strength ($\Delta\varepsilon$) of the two modes (M_1 and M_2) do not change significantly on application of the bias electric field up to 35 kV cm^{-1} (see figure 8). This indicates that mode M_1 of the SmA^* phase and mode M_2 of the SmC_α^* phase have similar natures. Furthermore, f_R for mode M_2 still lies in the high kHz region. Values of $\Delta\varepsilon$ (<12) and h (~ 0.06) are also small. These facts also support soft mode like behaviour of M_2 in the SmC_α^* phase. However, appreciable changes in the magnitude of f_R and $\Delta\varepsilon$ for mode M_3 have been observed with electric field of strength 35 kV cm^{-1} . The soft

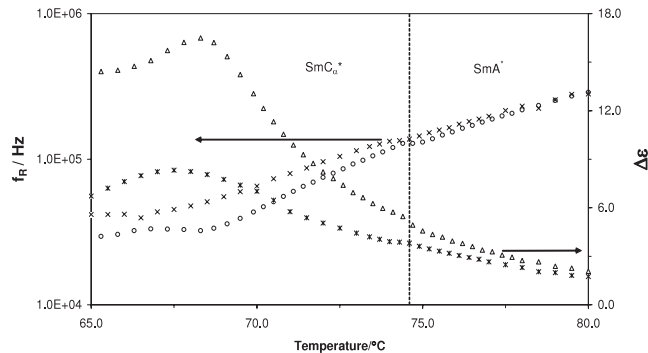


Figure 8. Temperature dependences of the relaxation frequency (f_R) and dielectric strength ($\Delta\varepsilon$) at bias electric field 35 kV cm^{-1} for SmA^* and SmC_α^* phases are shown by the cross and double symbol, respectively. The relaxation frequencies (open circle) and dielectric strength (open triangle) of the mode observed without a bias electric field are also shown in the figure for comparison.

mode is less affected by electric field far from the transition region and this rules out soft mode behaviour of M_3 . The temperature dependence of f_R for M_3 remains approximately constant but the value of h increases rapidly below 69.0°C . This is signature of a phase fluctuation (Goldstone like) mode in chiral tilted smectics. However, one may argue that, for the Goldstone like mode, the frequency should not be so high. But it should be noted that the relaxation frequency of the Goldstone mode in the ordinary SmC^* phase is inversely proportional to the square of the helical pitch. As the pitch in the SmC_α^* phase is found to be less than 100 nm [3, 12], it is expected that the frequency of the Goldstone like mode in SmC_α^* phase will be high in comparison to the usual SmC^* phase value.

4. Conclusions

- Thermodynamic, optical texture and dielectric studies prove the occurrence of SmA^* and SmC_α^* phases in the compound investigated.
- The single relaxation mode observed in the SmA^* phase has been identified as a soft mode on the basis of its temperature and bias field dependence.
- In the SmC_α^* phase, two different relaxation processes have been observed in different temperature ranges.
- Temperature, frequency and bias electric field dependent studies of dielectric parameters confirmed that the collective dielectric relaxation mode of the SmC_α^* phase behaves like a soft mode near the $\text{SmA}^*-\text{SmC}_\alpha^*$ transition. However, far from the transition, it behaves as a phase fluctuation (Goldstone like) mode.
- The experimental findings are in agreement with proposed theory for dielectric behaviour of the SmC_α^* phase.

Acknowledgments

One of the authors (MBP) wishes to thank the Department of Science and Technology, New Delhi, India, for financial assistance under a fast track project for young scientists

(SR/FTP/PS-14/2005). We sincerely thank Professor H Prakash, Head, Department of Physics, and Professor I M L Das, In charge, Impedance Spectroscopy Laboratory, Department of Physics, University of Allahabad, Allahabad, for their support.

References

- [1] Fukuda A, Takanishi Y, Isozaki T, Ishikawa K and Takezoe H 1994 *J. Mater. Chem.* **4** 997
- [2] Mach P, Pindak R, Levelut A M, Barois P, Nguyen H T, Huang C C and Furenlid L 1998 *Phys. Rev. Lett.* **81** 1015
- [3] Shtykov N M, Chandani A D L, Emelyanenko A V, Fukuda A and Vij J K 2005 *Phys. Rev. E* **71** 021711
- [4] Liu Z Q, McCoy B K, Wang S T, Pindak R, Caliebe W, Barois P, Fernandes P, Nguyen H T, Hsu C S, Wang S and Huang C C 2007 *Phys. Rev. Lett.* **99** 077802
- [5] Cepic M, Heppke G, Hollidt J M, Lotzsch D, Moro D and Zeks B 1995 *Mol. Cryst. Liq. Cryst.* **263** 207
- [6] Merino S, de la Fuente M R, Gonzalez Y, Perez Jubindo M A, Ros B and Puertolas J A 1996 *Phys. Rev. E* **54** 5169
- [7] Fafara A, Wrobel S, Haase W, Marzec M and Dabrowski R 2002 *Proc. SPIE* **4759** 151
- [8] Hoffmann J, Giesselmann F and Kuczynski W 2007 *Phase Transit.* **80** 841
- [9] Pandey M B, Dhar R, Agrawal V K, Dabrowski R and Tykarska M 2004 *Liq. Cryst.* **31** 973
- [10] Hou J, Schacht J, Giesselmann F and Zugenmaier P 1997 *Liq. Cryst.* **22** 409
- [11] Vaupotic N, Cepic M and Zeks B 2000 *Ferroelectrics* **245** 175
- [12] Pandey M B, Dhar R and Dabrowski R 2008 Amplitude and phase fluctuation modes in the smectic-C_a^{*} phase of an antiferroelectric compound *Liq. Cryst.* submitted
- [13] Douali R, Legrand C, Laux V, Isaert N, Joly G and Nguyen H T 2004 *Phys. Rev. E* **69** 031709
- [14] Pandey M B, Dhar R, Agrawal V K and Dabrowski R 2004 *Mol. Cryst. Liq. Cryst.* **414** 63
- [15] Pandey M B, Dhar R and Dabrowski R 2008 *Phil. Mag.* **88** 101
- [16] Pandey M B, Dhar R, Achalkumar A S and Yelamaggad C V 2007 *J. Phys.: Condens. Matter* **19** 436219
- [17] Cole K S and Cole R H 1941 *J. Chem. Phys.* **9** 341
- [18] Pandey M B, Dhar R and Dabrowski R 2006 *Ferroelectrics* **343** 83
- [19] Pandey M B, Dabrowski R and Dhar R 2007 *Physica B* **387** 25