

Soft Matter

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Experimental evidence of soft mode in smectic C_{α}^* phases

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Dielectric properties of chiral smectic liquid crystals characterised by the occurrence of the C_{α}^* phase were investigated in the frequency range 10 Hz – 1 MHz. In the range of existence of that phase the observed relaxation spectrum is composed of two kinds of mode, and not of the single one, as commonly thought. Phase modes of the Goldstone type coexist in it with an amplitude-type soft mode. The share of the soft mode in the global value of electric permittivity ϵ can be dominant and attain 90%. A possible explanation of that effect is sought in the similarity to chiral phases of deVries type.

1 Introduction

Dielectric spectroscopy is one of the most effective techniques of investigation of dipolar ordering and dynamics of collective molecular processes in liquid crystal (LC) materials. The existence of a collective response of the molecules to external electric field is the result of a long-range dipolar ordering characteristic of ferroelectric materials.

The presence of the spontaneous polarisation in the smectic layers of the ferro-, ferri- and antiferroelectric phases of liquid crystals leads to a unique characteristic dielectric response of every polar phase. Taking advantage of this feature, the identification of the phases present in new materials can be performed by examining their dielectric properties as a function of frequency. The details of the structure of smectic phases characterised by a long-range dipolar order still remains a mystery. Dielectric studies can provide information on this subject. Currently, the best described and understood is the dynamics of collective modes in the ferro- and paraelectric phases of chiral smectics.¹

In the ferroelectric phase of the chiral smectic C^* two basic collective modes appear:

- the mode associated with the variation in the tilt angle of the molecules in the smectic layer. This is the amplitude mode often referred to as the soft mode;
- the mode associated with the azimuthal variations in the tilt direction of the molecules in the smectic layer. This is the phase-type mode called the Goldstone mode.

A more complex picture of modes is expected in the antiferroelectric phase of chiral smectics.² The basic element of the

structure of the antiferroelectric phase is a pair of two adjacent smectic layers, with the tilt directions of the molecules differing almost exactly by an angle of 180° . The tilt directions are ordered in a helical manner. Due to the existence of the helicoidal order, the polarisation in adjacent layers does not compensate completely. On the basis of this characteristic, the theory foresees four modes² in such a structure: two phase modes and two amplitude modes. The phase modes are associated with variations in the azimuthal angles of the tilt directions of in-phase or anti-phase oscillations of molecules, while the amplitude modes show variations in the tilt angles of molecules in neighbouring smectic layers, which also can run in-phase or in anti-phase. The predictions of theory and the measurement results on the ferroelectric and antiferroelectric chiral smectics remain in satisfactory compliance; nevertheless, the interpretation of experiments on the smectic C_{α}^* phase is still controversial. This phase is one of the sub-phases observed in antiferroelectric liquid crystals.^{3,4} Their occurrence is not always reproducible.⁵ The existence of sub-phases can depend on many factors such as the content of chemical impurities, interactions with surfaces or the sample history.⁵ The smectic C_{α}^* phase appears only in materials of high optical purity, that is, those which lack even a minor admixture of the enantiomers of opposite handedness.⁶

According to theoretical predictions, in the smectic C_{α}^* phase, two modes – the soft mode and the Goldstone one, like in the ferroelectric phase, can be observed. However, in many experimental investigations, a single collective mode is observed,^{7–11} similarly to the smectic A phase. In some studies, opinion is expressed that it has an amplitude character (soft mode),^{7,11} while in the other ones it is considered as a phase-type Goldstone mode associated with the perturbation of the helical structure.^{8–10} The answer to the question whether the observed mode is of the phase-type or the amplitude-type one is important, because it would resolve the dispute about whether or not the helical order with a very short

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pitch is an element characterising the C_{α}^* phase.

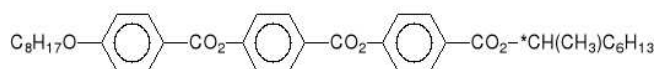
The goal we have set starting this research was to gather the most comprehensive data on the dielectric properties of that phase with the hope that they will contribute to the clarification of the existing doubts.

2 Experimental

We used a measuring system consisting of an Impedance Analyzer 4192A from Hewlett-Packard and a phase-sensitive voltmeter Lock-In SR 850 from Stanford (analysing the electrooptic effect signal recorded by the photodiode with preamplifier from FLC Electronics) that allowed us to make simultaneous measurements of the complex electric permittivity and the electrooptic effect as a function of frequency and temperature. The frequency range for common measurements was limited by the design of the Lock-In voltmeter to the range of 5 Hz - 100 kHz. However, measurements of dielectric permittivity could be carried out in the frequency range from 5 Hz to 5 MHz. The measurement cells were placed in a modified microscopic hot stage Mettler FP 82 HT. The temperature was stabilised using the home made "Temperature Controller" with the accuracy of ± 0.01 K. The functions of temperature control, variations in the measurement frequency and experimental data acquisition were controlled by a suitably programmed computer. The investigated samples of liquid crystals were placed in commercial measuring cells from EHC, Linkam and AWAT with thicknesses of 5, 10 and 25 μm with the semitransparent electrodes of indium-tin oxide (ITO) assuring planar ordering through appropriately crafted surfaces.

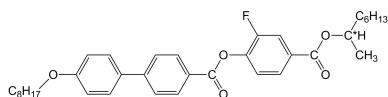
Three liquid crystal materials were investigated:

1. 4-(1-methylheptyloxycarbonyl) phenyl 4-(4-octyloxyphenylcarbonyloxy) benzoate, described in the current work with the abbreviation D17, with the following molecular structure:



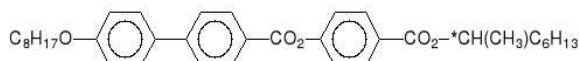
SmA* 95 °C SmC $_{\alpha}^*$ 87 °C SmC $_{\beta}^*$ 82 °C SmC $_{\gamma}^*$

2. D16



SmC $_{\beta}^*$ 43 °C SmC $_{\alpha}^*$ 56.1 °C SmA*

3. MHPOBC



SmA 122.1 °C SmC $_{\alpha}^*$ 120.7 °C SmC* 119.3 °C SmC $_{\gamma}^*$
118.3 °C SmC $_A^*$

The choice of these compounds was decided, since the existence in their phase diagram of the temperature range permitting the appearance of the phase SmC $_{\alpha}^*$ was not challenged in any of our observations.

3 Results

As a rule, in every LC investigated, the shape of $\epsilon = f(T)$ depends on the direction of change in temperature. The thermal hysteresis $\epsilon(T)$ is well seen in Fig. 1, showing the temperature dependence of the real component of electric permittivity ϵ' , measured at a frequency of 110 Hz. In all materials examined, the occurrence of the smectic A phase and smectic C_{α}^* phase does not depend on the direction of temperature changes. However, in the D16 and D17 materials, the neighbourhood of the SmC $_{\alpha}^*$ phase from the side of lower temperatures depends on whether the temperature during the measurements is lowered or raised. The order of appearance of phases on cooling is in both materials identical: isotropic phase - SmA phase - SmC $_{\alpha}^*$ phase - SmC $_{\beta}^*$ phase (with compensated polarisation). In MHPOBC and D17, the succession of various phases that appear on heating is different. From the low-temperature side, the phase SmC $_{\alpha}^*$ is adjacent to the SmC* phase with high dielectric permittivity masking the phase transition point.

In MHPOBC, like in D16 and D17, the occurrence of the SmA phase and the SmC $_{\alpha}^*$ phase does not depend on the direction of temperature changes. From the side of lower temperature, at both directions of temperature change, the SmC $_{\alpha}^*$ phase is adjacent to the SmC* phase with non-compensated polarisation. Taking into account the type of behaviour of the D16 and D17 materials, we decided that most of the data undergoing further analysis came from the measurement cycles performed during cooling from SmA phase.

At the core of our interest in the dielectric properties of the phase SmC $_{\alpha}^*$ was the desire to understand why does it behave more like the paraelectric SmA phase, rather than like the ferroelectric SmC* one, as reported in numerous papers.⁷⁻¹² This is surprising, because it seems to be contrary to the expectations based on the structural analysis. In fact, it only proves that two assumptions made in theoretical models are not exactly fulfilled; these can be verified by dielectric relaxation investigations:

- Since the SmC $_{\alpha}^*$ phase has to be ferroelectric, it should be characterised by a helical structure, which implies the need for the presence in the dielectric response of two modes – of phase- and amplitude-type.

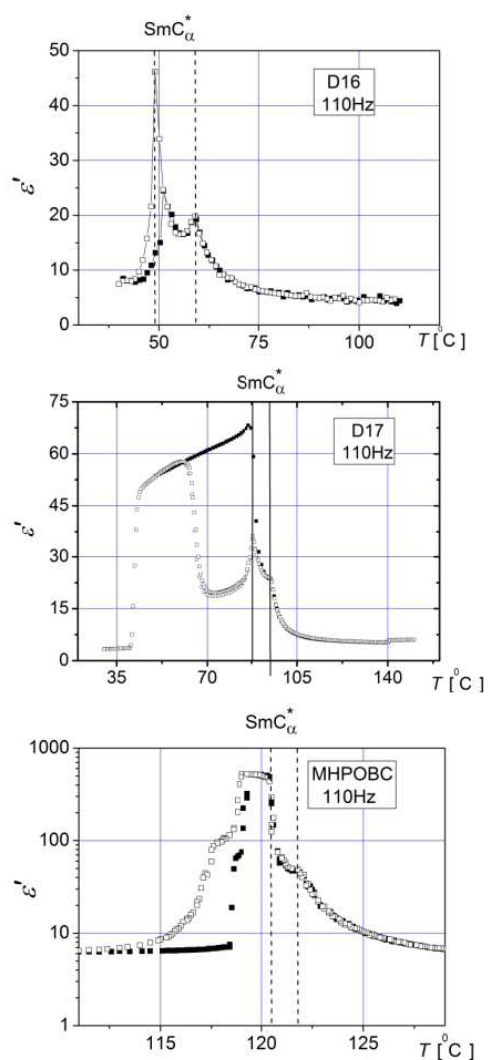


Fig. 1 Thermal hysteresis of the real component of electric permittivity ϵ' . Heating cycle - full symbols, cooling cycle - open symbols. Vertical broken lines mark the temperature range of existence of the SmC_α^* phase

- Since the SmC_α^* phase has to be optically uniaxial, its helical structure must have a very short pitch, which implies a significant reduction in the relaxation time of the phase mode.

Since only one mode is recorded in the SmC_α^* phase, the conclusion would be justified that it is either of a phase-type (which would confirm the existence of a helical arrangement) or of an amplitude-type - soft mode, which would be a strong argument in denying the necessity of the helix formation in the structure of that phase.

3.1 Dielectrically active modes in SmC_α^*

The simplest and fairly reliable way to verify the existence of the soft mode is to determine whether, and within which range of temperature, the Curie-Weiss law is met in the investigated phases. The application of this law to ferroelectric liquid crystals requires a minor modification. Due to the fact that the value of the permittivity of the paraelectric phase is high relative to the maximum, it cannot be neglected. The real components of the dielectric permittivity ϵ' as a function of temperature, recorded at a frequency lower than the range of the slowest relaxation mode, should become the fitting parameters.

In our study, these were the results of a series of measurements conducted during the cooling at a frequency of $f = 110$ Hz of the measuring electric field.

In the calculations we applied the equation in the following form:

$$\epsilon = \frac{C}{T - T_C} + \epsilon_T, \quad (1)$$

where C denotes the Curie-Weiss constant, T_C - Curie temperature and ϵ_T - the "background" electric permittivity. The quantities listed were the parameters in the fitting procedure. The data taken for two temperature ranges were subjected to two separate attempts to fit:

1. That comprising the SmA phase - from the temperature of the phase transition $\text{SmC}_\alpha^* - \text{SmA}$ to the isotropic phase boundary,
2. That covering the widest possible range of temperature of the SmC_α^* phase existence - from the phase transition $\text{SmC}_\alpha^* - \text{SmC}_\beta^*$, or in case of MHPOBC - the transition $\text{SmC}_\alpha^* - \text{SmC}^*$.

The results of the fittings are shown in Fig. 2

and in Tab. 1. The data presented in Fig. 2 show that in the

Table 1 Quantities found by the fitting procedure

	D17	D16	MHPOBC
$\text{SmA } \Delta T$	97 – 140 °C	59 – 98 °C	121.9 – 135 °C
C	39.40	105.25	24.69
$T_C^{(2)}$ [°C]	95.59	53.66	121.47
$\epsilon_T^{(2)}$	5.13	3.20	3.40
$\text{SmC}_\alpha^* \Delta T$	90.3 – 95.3 °C	49 – 57 °C	120.4 – 121.5 °C
C	38.17	27.07	25.11
$T_C^{(1)}$ [°C]	87.01	48.91	120.27
$\epsilon_T^{(1)}$	21.97	15.55	29.11

examined materials the Curie-Weiss law is well met. This applies to the whole range of temperature of SmA phases (Fig. 2) and a large part of the range of SmC_α^* phases (Fig. 2).

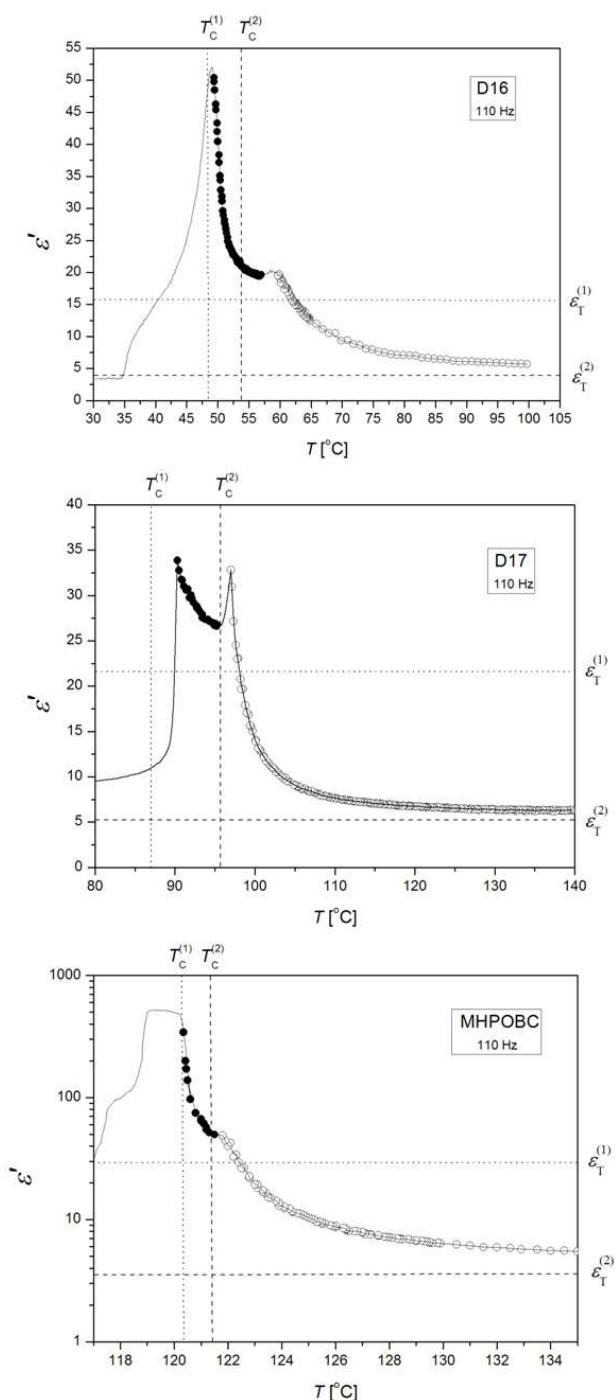


Fig. 2 The applicability range of the Curie-Weiss law. D16 (top), D17 (middle), MHPOBC (bottom). Open symbols mark the SmA phase data, full symbols – the SmC_α^* phase ones used in the fitting process. Full line marks the ϵ experimental data outside the fitting range. Broken lines mark the calculated values of fitting parameters (see Tab. 1)

The contents of Tab. 1 can be summarised by the following observations:

- background permittivity ϵ_T calculated for the SmA phase is of the order of several units, which is a typical contribution originating from the non-collective molecular motions;
- background permittivity ϵ_T values calculated for the SmC_α^* phase represent 6 – 63% of the total ϵ value. This can indicate that in addition to the soft mode in SmA, other collective molecular processes contribute to ϵ in SmC_α^* . This question will be commented on in more details in Section 4;
- the values of $T_c^{(2)}$ calculated for phase transitions SmA – SmC_α^* are lower than the observed phase transition temperatures in all materials investigated;
- the values of $T_c^{(1)}$ calculated for phase transitions $\text{SmC}_\alpha^* - \text{SmC}_\beta^*$ in D16 and D17 are also lower than the observed phase transition temperatures. For the phase transition $\text{SmC}_\alpha^* - \text{SmC}^*$ occurring in MHPOBC the calculated $T_c^{(1)}$ value agrees within experimental accuracy with the recorded one.

3.2 Results obtained by dielectric spectroscopy

As mentioned in the Introduction 1, on starting with these studies we hoped that the results obtained would allow us to take part in a debate if the single mode in the SmC_α^* phase, mentioned in literature, is a phason or an amplitudon. Applying the Curie-Weiss law to the analysis of the results of dielectric measurements we knew that we could find areas of its applicability in the range of existence of the SmA phase. The possibility that they can also be registered in the SmC_α^* phase was a hypothesis which, as shown in the current work, we were able to verify in a positive way.

The unexpected result of this part of the study showed the scale of the soft mode contribution to the global value of permittivity ϵ . The percentages of contributions to ϵ , divided between the share of the soft mode (SM) and the rest (without specifying its nature) are presented in Tab. 2. Our conclusion

Table 2 Contributions to dielectric permittivity ϵ in the SmC_α^* phase

Contributions to ϵ	D17	D16	MHPOBC
Total	35 (100%)	50 (100%)	500 (100%)
SM	13 (37%)	38 (76%)	470 (94%)
Rest	22 (63%)	12 (24%)	30 (6%)

following the results obtained was that the SmC_α^* phase should

be characterised by the presence of two modes. The opinion that it is otherwise, suggested by earlier investigations of the material D17,⁷⁻¹² could follow the fact that due to close values of the relaxation times the modes could not be separated. It became to us an incentive to perform dielectric spectroscopy studies and accompanying calculations for many times, thus reducing the risk of errors.

Dielectric dispersion was registered in all liquid crystalline phases of materials studied (Figs. 3, 4 and 5).

According to common usage, by analysing the results of measurements of dielectric permittivity as a function of frequency, we have described the dielectric absorption composed of a number of bands as a sum of the processes of Cole-Cole type:¹³

$$\epsilon' = \epsilon_{\infty} + \sum_n \frac{\Delta\epsilon_n}{1 + i(\omega\tau_n)^{1-\alpha}} \quad (2)$$

where $n = 1, 2, 3 \dots$ marks different modes, ϵ_{∞} is electric permittivity at high frequencies, ω - the angular frequency of the measuring electric field, τ_n - relaxation time, and $\Delta\epsilon_n$ - the amplitude of the n -th mode. The parameter α describes the distribution of relaxation times. The amplitude and relaxation time of every mode was calculated by matching the real and imaginary parts of permittivity using the "Relax" software created by J. Małeckı.¹⁴ The advantage of this software is that it allows the simultaneous adjustment of each part, ϵ' or ϵ'' , of the dielectric permittivity, thus reducing the margin of ambiguity, which is crucial in the analysis of many partially cross-covering bands. During the calculations, we have found that the parameter α is small and does not exceed the value of 0.1. We decided, therefore, that the fits will be carried out using a Debye-type model ($\alpha = 0$), increasing its reliability by reducing the number of matched parameters. The results of the calculations, based on the results of measurements obtained during cooling, are presented in Fig. 6.

Focused on the properties of the dielectric properties of the phase SmC_{α}^* , we were mainly interested in the temperature range covering this phase and areas of phase transitions to the phases directly adjacent to it along the temperature axis.

Figure 6 (middle) shows the results for the material D17. The simplest situation was recorded in the range of SmA phase (97.5 - 110 °C): A single mode, identified as the soft one, appears there. This mode also extends to the whole range of the phase SmC_{α}^* . Within that phase, it is accompanied by yet another mode with an amplitude of the same order of magnitude (10 - 20), but with a longer relaxation time. It was recorded down to the limiting temperature of 60 °C. It is identified as a phase-type Goldstone mode describing the dynamics of the ferroelectric phase SmC^* . In the vicinity of 87 °C, the mode identified as a soft one vanishes. It is replaced by a new one of a very low amplitude (2 - 3) and the relaxation time of the order of μs recorded up to 75 °C in the whole range of existence of the phase SmC_{β}^* .

Following the authors of ref.¹² we admitted that the phase, which we call SmC_{β}^* , observed on cooling the phase SmC_{α}^* of the material D17, represents an area of a metastable coexistence of the ferroelectric phase SmC^* and the antiferroelectric phase SmC_{α}^* . Thus, the low-amplitude mode observed in the range of temperature 87 - 75 °C is identified as the antiferroelectric equivalent of the Goldstone mode.

A complex picture of the dispersion is seen also in the dielectric material D16 (Fig. 6 (top)). In the SmA phase (59 - 100 °C), like in the material D17, a single mode was registered, which has a continuation in the SmC_{α}^* phase; we identify it down to 45 °C as a soft mode (SM). From the beginning of the range of existence of the phase SmC_{α}^* (at about 59 °C) down to the end of the measuring range (45 °C) the SM mode is accompanied by the second one with a lower amplitude (approx. 10) and relaxation time longer by one order of magnitude. We assign to it the characteristics of the phase Goldstone mode.

The results of calculations of the dielectric dispersion of MHPOBC are also shown in Fig. 6 (bottom). In the range of the existence of the SmA phase, a single (soft) mode SM was recorded. Like in the material D16, it was observed up to the temperature terminating the measurement range (117 °C).

From the initial temperature of the SmC_{α}^* phase, to the end of the range of existence, a second mode with an amplitude by one order of magnitude lower and a relaxation time longer by almost two orders of magnitude was registered. It is identified as a phase-type Goldstone mode.

3.3 Evolution of dielectric relaxation times of SmC_{α}^* phases

In this part of the discussion an attempt will be made to verify the thesis of a considerable shortening of the relaxation time of the phase mode of the SmC_{α}^* phase. According to the theoretical predictions of the generalised Landau model,¹⁵ the relaxation time τ of the phase-type Goldstone mode is proportional to the square of the helix pitch p . The expected pitch in the helical structure of the SmC_{α}^* phase, expressed in terms of the number of smectic layers with a thickness of about 4 nm each, ranges from a few to several dozen. This means that the quantity p in that phase should fall within the range of 10 - 100 nm. On the other hand, the average values of the parameter p in the SmC^* phases are comprised within the range of several hundred to several thousand nm and are from 10 to 100 times longer. Given this estimate, the transition from the SmC^* phase to the SmC_{α}^* one should be accompanied by a shortening of the relaxation time τ by two to four orders of magnitude.

In the studied materials, the relaxation times τ of the Goldstone modes in the SmC^* phases are about ten times longer than those recorded in the SmC_{α}^* phases. If assumed that the

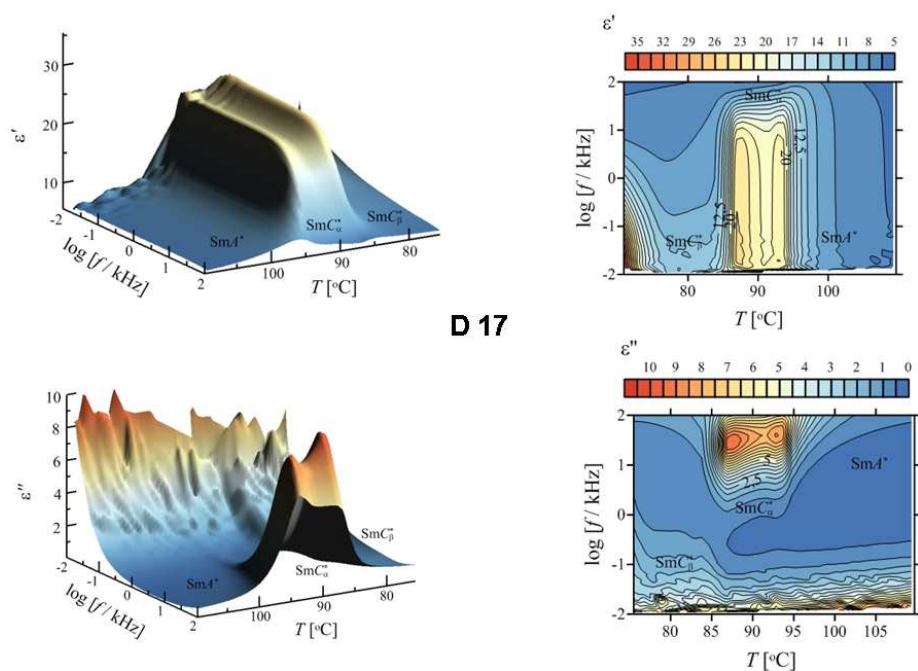


Fig. 3 Material D17. Contour and spatial presentation of the real (top) and imaginary (bottom) permittivity components as a function of temperature and frequency measured during the cooling cycle

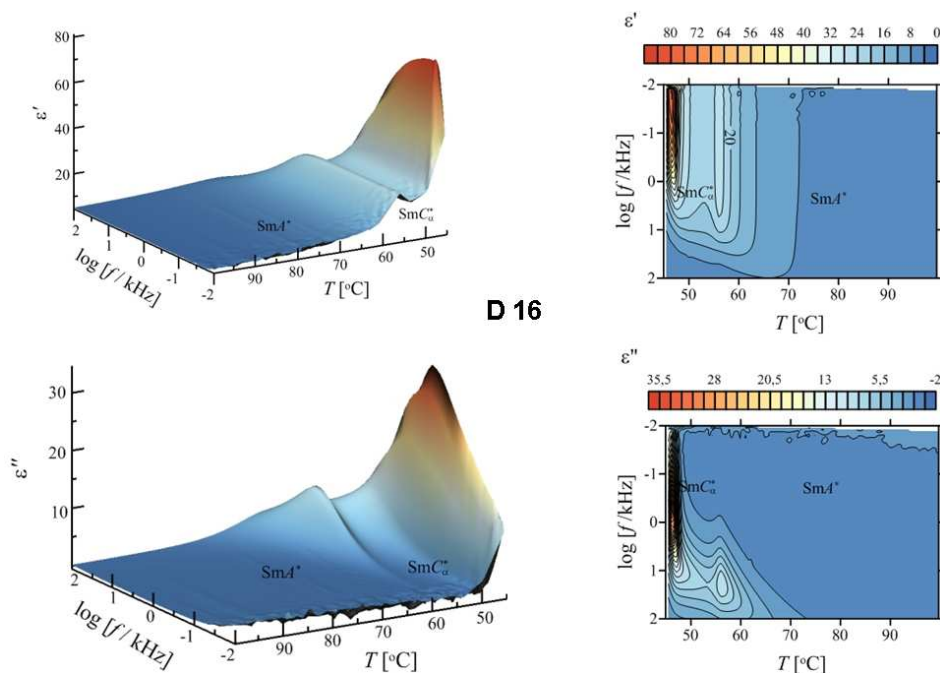


Fig. 4 Material D16. Spatial and contour presentation of the real (top) and imaginary (bottom) permittivity components as a function of temperature and frequency measured during the cooling cycle

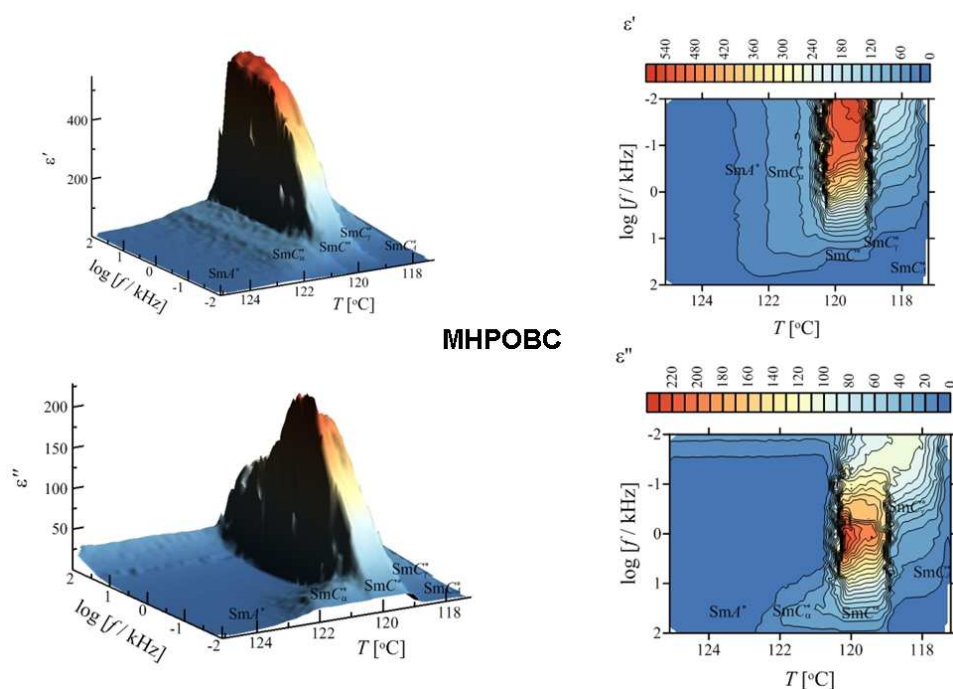


Fig. 5 Material MHPOBC. Spatial and contour presentation of the real (top) and imaginary (bottom) permittivity components as a function of temperature and frequency measured during the cooling cycle

relaxation times characterising the SmC_α^* phase describe the azimuthal mode, then according to that principle it might be considered that the helix pitch p in the SmC_α^* phase is three times shorter than in the SmC^* phase. Thus, the shortening would be limited to the range of typical changes observed during the heating of ferroelectric smectic C^* phase to the paraelectric SmA one.

4 Discussion

The presence of the soft mode in chiral smectics exhibiting the dipolar long-range order is their natural attribute. Foreseen in the theoretical work by R. Blinc,¹⁶ it was registered already in first studies on the chiral ferroelectric, DOBAMBC liquid crystal¹⁷ using dielectric methods. It was found that, in agreement with ref.¹⁶, in the paraelectric SmA phase, this mode brings to the global value of permittivity ϵ a weak but noticeable contribution meeting the Curie-Weiss law in temperatures up to approximately 1°C above the phase transition $\text{SmC}^* - \text{SmA}$.¹⁷ The maximum share of the SM of 0.5, accounted for approximately 10% of the contribution to ϵ from non-collective molecular motions. The results of numerous subsequent studies on ferroelectric properties of the SmC^* and SmA phases by dielectric spectroscopy have shown that such a "trace" input with respect to the amplitude is typical. The

relaxation times of SM determined in the course of the current studies in the SmA phase were located within the range from 10^{-6} to 10^{-8} s.² Similarly, low values of the SM amplitude were observed in the ferroelectric SmC^* phase. In practice, its recording is limited to a narrow range of temperatures near the phase transition $\text{SmC}^* - \text{SmA}$. This is due mainly to the fact that the relaxation times become too short and do not fall within the standard range of measurement frequencies that does not generally exceed 10 MHz.²

A completely different situation was observed in the current experiment. The SmA phase is adjacent to the SmC_α^* phase. The contribution of the SM mode to the value of ϵ in the SmA phase is dominant. Its influence is recorded in the entire temperature range of existence of the phase. The maximum contribution of SM to ϵ , recorded near the $\text{SmC}_\alpha^* - \text{SmA}$ phase transition temperature, relative to the rest representing the share of the non-collective molecular motions, is presented in Tab. 3. The dominant role of the SM mode

Table 3 Contributions to dielectric permittivity ϵ in the SmA phase

Contributions to ϵ	D17	D16	MHPOBC
Total	32 (100%)	20 (100%)	50 (100%)
SM	27 (84%)	16 (80%)	46 (92%)
Rest	5.13 (16%)	3.2 (20%)	3.4 (8%)

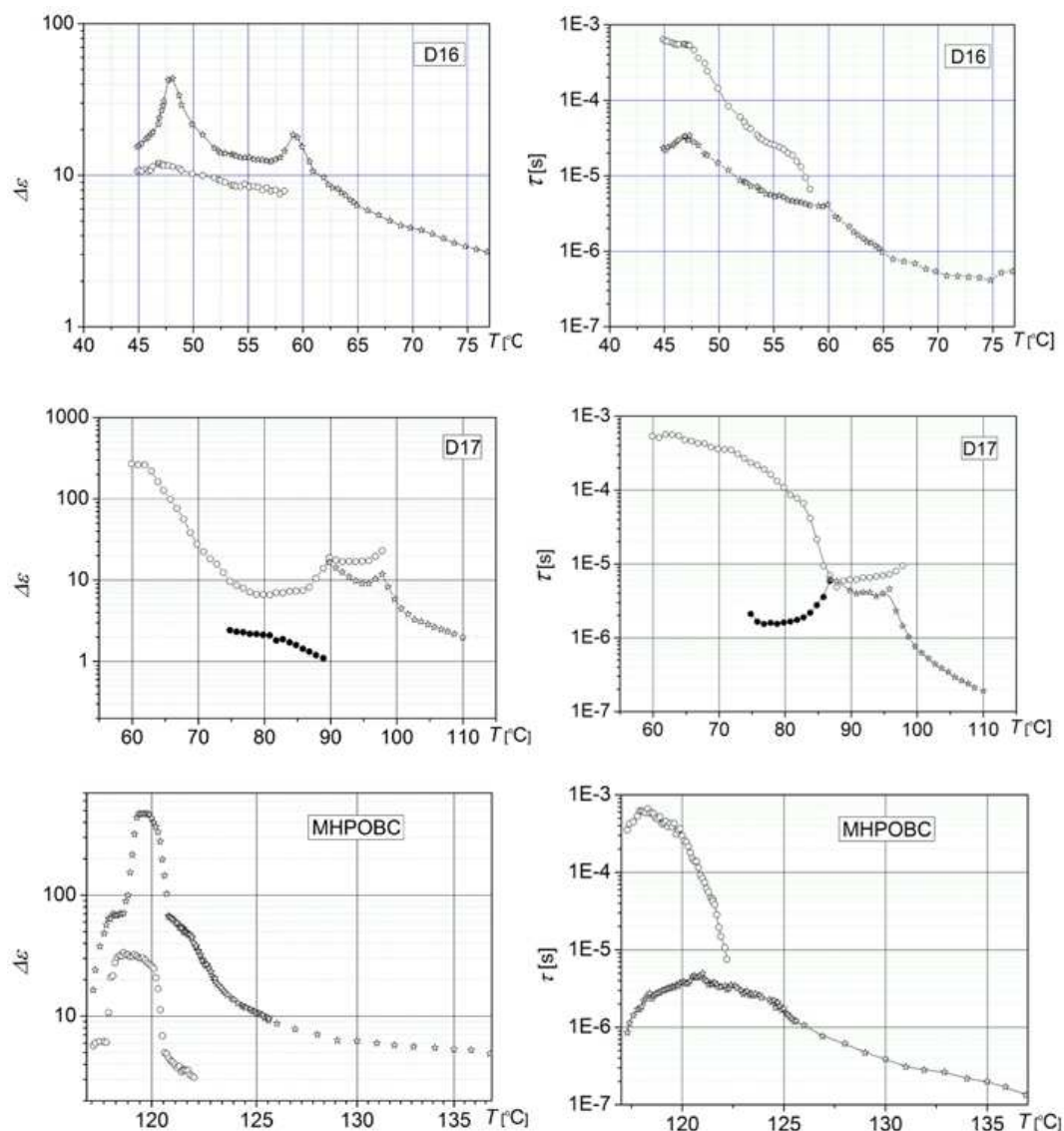


Fig. 6 Temperature dependence of the amplitudes of the dielectric shares $\Delta\epsilon$ (left) and of the relaxation times τ (right) of D16 (top), D17 (middle), and MHPOBC (bottom). Open asterisks indicate the share of the soft mode (SM), open circles – that of the Goldstone mode, closed circles – that of the antiferroelectric Goldstone mode

in the SmA phase, a wide temperature range in which it is registered and meeting the Curie-Weiss law in almost whole range of phase existence are the characteristics considered as typical for the deVries-type liquid crystals made of chiral molecules.¹⁸ As a consequence of small changes in the thicknesses of the smectic layers at the phase transition from SmC* ferroelectric phase to the paraelectric SmA one, the molecules in the latter remain tilted. The phases SmC* and SmA differ not by the lack of the tilt of the molecules in the smectic layer, but by the absence of the order in the tilt directions of molecules. To obtain the effect of increasing the dielectric

permittivity in the chiral SmA deVries-type phase one does not need to force the molecules to tilt, but just to order their tilt directions.¹⁸ In addition to those similarities characterising the investigated liquid crystals and deVries-type materials, there is yet another one – the temperature dependence of the smectic layer thickness. It is presented in Fig. 7. Data for D16 and D17 are derived from our X-ray diffraction experiments. The graph for MHPOBC was drawn on the basis of data taken from ref.¹⁹. Changes in the thicknesses of the smectic layers at the transition from the SmC* phase to the SmA one, as shown in Fig. 7, which account for less than 4% of the total

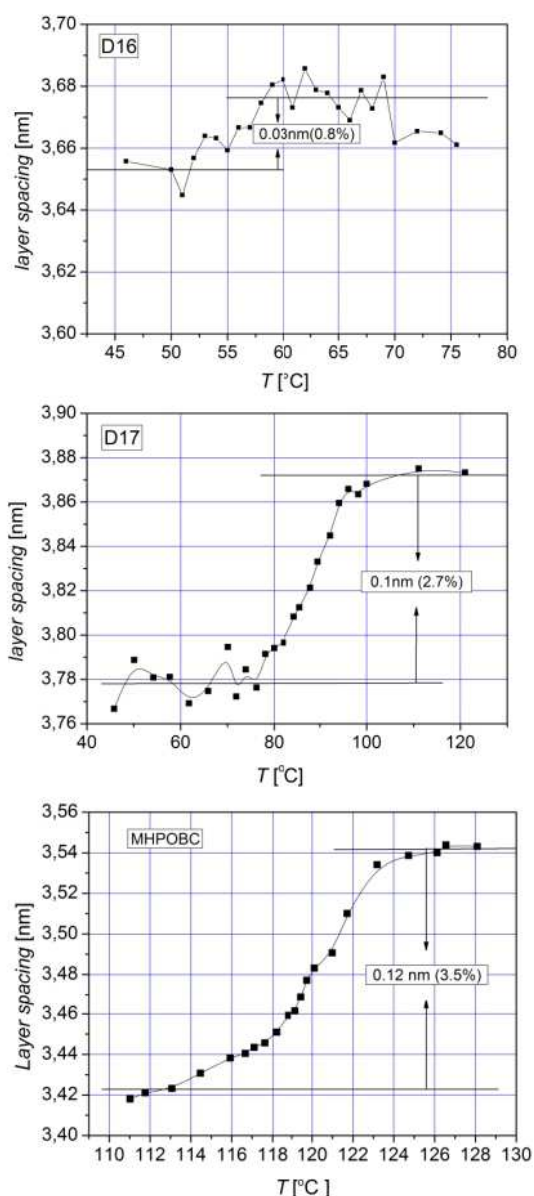


Fig. 7 Thickness of smectic layers as a function of temperature: D16 (top), D17 (middle) and MHPOBC (bottom)

value, suggest that in this respect the deVries character of the SmA phases of the materials studied is complete.

The question remains, how to explain the large contribution of SM to the dielectric permittivity ϵ of the SmC_α^* phase. In the temperature range corresponding to that phase, in all the materials examined, a soft amplitude-type mode has been found to coexist with the phase-type Goldstone one. That is, since the phase mode is registered, the helicoidal ordering should occur. However, such an ordering should not suppress

the possible amplitude vibrations. Such a phase would mediate between the SmA phase of deVries type and the helicoidal SmC^* one. One of the possible ways to achieve such a compromise would be the premise that the phase SmC^* fulfils the following points:

1. in the smectic layers, the molecules tilt slightly differs from that existing in the SmA phase due to no change in their thicknesses;
2. the phases differ in that in the one in SmC_α^* the tilt directions of the molecules are more or less ordered – a single layer as a whole having the polarity uncompensated;
3. the distribution of directions of polarisation of the individual layers is isotropic, but with the possibility of local compensation by creating short sections of the helix;
4. there is no possibility to create a helix comprising the whole volume.

Studying a material that meets those conditions by dielectric methods would bring the chance to make observations such as those obtained by us. It may therefore happen that the SmC_α^* phase is such an indirect link. The fact that we come to it from the "traditional" chiral smectics C^* suggests the name "exotic" variety of the SmC^* phase or, alternatively, the SmC^* phase of deVries type.

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