

**Behavior of the helix in some chiral smectic- $C^*$  liquid crystals**

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In spite of numerous papers dedicated to the subject, the behavior of the helical pitch in the smectic  $C^*$  phase near the smectic A phase is still controversial. In particular, it is not clear to what extent the measured pitch values are influenced by surface effects. In order to shed light on this problem, careful pitch measurements have been performed using different methods and sample preparations. We have found that the diffraction of light on planar-oriented samples may give incorrect pitch results because of strong influence of the surfaces and possibly of the sample texture on the helical structure. We have demonstrated that using appropriate preparation of samples the bulk properties of the helix can be determined. It has been found that a maximum of pitch can indeed occur but then only when very close to the transition point smectic  $C^* \rightarrow$  smectic A (about 0.1 K). The results of helical pitch measurements have been compared with predictions of theories.

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**I. INTRODUCTION**

Smectic liquid crystals build of chiral rodlike molecules which long axes are, on average, not perpendicular to the smectic layers plane, possesses long-range dipole order in each smectic layer. Depending on mutual orientation of the resulting dipole moments of the layers (i.e., their spontaneous polarization vectors), a material can exhibit either ferroelectric, ferroelectric, or antiferroelectric properties [1]. The chirality of molecules, being the necessary condition for the dipole order, causes simultaneously the change in the tilt direction in successive layers. The tilt direction rotates continuously along the layer normal resulting in the helical structure, described by the wave vector  $q=2\pi/p$  where  $p$  is the helical pitch.

The helical pitch belongs to the most important material parameters of chiral liquid crystals. Its behavior, especially the temperature dependence, can be a convenient test for the correct thermodynamic description and for general theories of the smectic  $C^*$  phase and can help to understand the smectic  $C^*$ -smectic A transition [2]. It is also the decisive factor for determination of the flexoelectric polarization, which plays an important role in displays operating in the deformed helix mode. Recently, the knowledge of the flexoelectric polarization (and, consequently, of the pitch behavior) has become even more important as their role in producing various modifications of the smectic  $C^*$ -phase (subphases) was theoretically recognized [3,4]. Hence, the knowledge of the behavior of the helical pitch  $p$  is important for design of displays and other electro-optic devices. It determines the electro-optic properties, the threshold magnitude, and the speed of switching.

Papers dealing with pitch measurements have been quite frequent (see, e.g., [5–11]). However, the measurement of helical pitch in smectic liquid crystals belongs to the most difficult among all measurements of material constants [12] of tilted smectics. A few measuring methods are used [6–8]; however, the results are often quite controversial. Apart from

numerical values, the character of the temperature dependence has been found to be similar in almost all cases. At low temperatures, far from the  $C^*$ -A transition, the pitch has been found to increase with temperature up to a few degrees below the transition and then decrease to low values. Different behavior is observed at the transitions to other phases, e.g., to the smectic  $C_\alpha^*$  phase [13] or to twist grain-boundary (TGB) phases [14], but it will not be discussed here.

Many attempts have already been made to explain the temperature dependence of the helical pitch [15–19]. All theoretical models explained quite well the shape of  $p(T)$  dependence. However, in majority of cases the agreement was only qualitative. The only attempt to show the quantitative agreement has been demonstrated in Ref. [2] for classic ferroelectric liquid crystal DOBAMBC. However, even in this case the agreement between theory and experiment, although quite good at low temperatures, failed at the transition to the smectic A phase. Hence, up to now no convincing decision can be made concerning the explanation of the helical pitch behavior in the smectic  $C^*$  phase. Unfortunately, sufficiently reliable experimental data, which can be used for testing the theories, are not available. In most cases the pitch has been measured with the diffraction method using planar-oriented samples (the smectic layers perpendicular to the glass plates). This type of alignment is usually achieved by proper surface treatment and/or by use of a magnetic field. Normally, in these cases the interaction of liquid crystal molecules with the surface is strong. Therefore, in most cases the experimental data suffer from an error that is the consequence of neglecting the surface interactions.

We will demonstrate that this error can be surprisingly large—so large that it makes the comparison of theory and experiment impossible. On the other hand, there is no theory, which takes into account the influence of surface interactions on the helical structure. Thus, it turned out that there were no experimental data, which could be properly compared with existing theories. The aim of this paper is to supply such experimental data. In this paper we will critically compare some measuring methods and results obtained for some ferroelectric liquid crystals. These results will allow us to draw practical conclusions on the methods for correct mea-

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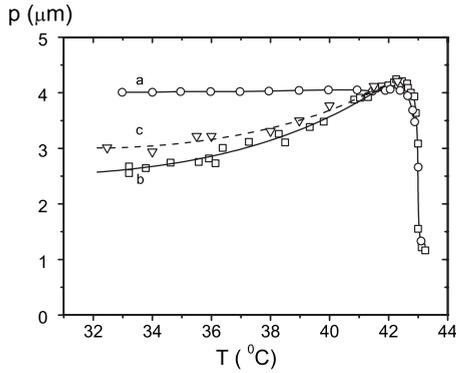


FIG. 1. The temperature dependence of the helical pitch measured in planar samples of C8 using the diffraction method. (a) circles: sample thickness 20  $\mu\text{m}$ , heating and cooling; (b) squares: sample thickness 110  $\mu\text{m}$ , heating; and (c) triangles: sample thickness 110  $\mu\text{m}$ , cooling.

surement of helical pitch in bulk samples of chiral smectic liquid crystals. The impact of the obtained results on the applicability of different theoretical models of the smectic  $C^*$  phase will be also discussed.

## II. EXPERIMENT

In this study, we investigated three materials having quite different molecular structure: 4'-methylbutyloxy phenyl-4-octyloxybenzoate (abbreviated C8 here), 4-(2,3-epoxyhexyloxy) phenyl-4'-decyloxy benzoate (Epoxy) from Aldrich, and 4-(2'-methylbutyl)-phenyl 4'-n-octyl-biphenyl-4-carboxylate (CE8) from BDH. We carried out diffraction experiments in both homeotropic and planar-oriented samples. A good planar orientation with only a small number of defects was achieved by rubbing the glass plates after coating with polyimide and, with a final very slow cooling, the sample ( $\sim 0.01$  deg/min) from the isotropic to the smectic A phase. The sample thickness varied between 20 and 200  $\mu\text{m}$ . The experimental results obtained using the diffraction method during heating were typical as shown in Fig. 1 for C8 samples of thickness 20 and 110  $\mu\text{m}$ .

The results for the 200- $\mu\text{m}$ -thick sample were less accurate due to inferior alignment quality but within the experimental accuracy the same as these for the 110  $\mu\text{m}$  sample. Upon cooling, the results for the 110  $\mu\text{m}$  sample at low temperatures were higher by about 20% than these at heating (broken line in Fig. 1). The outcome is similar to that from Ref. [7]: the experimental data depend on sample thickness. Together, the results clearly demonstrate the influence of surface interaction. The presence of the temperature hysteresis suggests the presence of an effect of pinning of molecules at surfaces and makes the interpretation of experimental data difficult. Anyway, the presence of hysteresis proves that at least one of the measuring runs is incorrect. In thin samples the pinning is so strong that the temperature changes do not appear at all. Near the phase transition  $C^*$ -A\* both the hysteresis and the dependence on thickness are small.

In homeotropically oriented samples the pitch investigations were carried out using two methods:

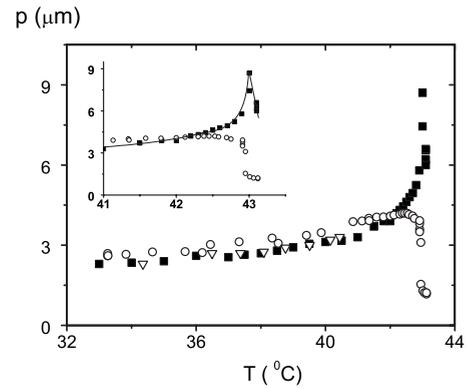


FIG. 2. The temperature dependence of the helical pitch measured in a homeotropic sample of C8 using the Cano method (full squares) and spectroscopic method (open triangles) for the cell 140  $\mu\text{m}$  thick. The results of diffraction experiment obtained in 110  $\mu\text{m}$  thick planar sample (open circles) are shown for comparison. The inset displays data for the temperature range close to the phase transition.

(i) measuring the wavelength of the selective reflection with an IR spectrometer;

(ii) measuring in a wedge-shaped sample the distance between a kind of “dislocation lines” appearing in the periodic twist structure (a modification of the Cano method [20], usually used for cholesteric liquid crystals).

To achieve the varying thickness we placed the sample between a glass plate and a lens of known radius of curvature. The surfaces of the plate and of the lens were coated with a surfactant (cetyl trimethyl ammonium bromide-CTAB) to get homeotropic orientation. The ordering of the  $\mathbf{c}$  director on the glass surfaces needed for observation of Cano disclinations was achieved by a gentle shearing. The observed disclinations separate areas in which the rotation of the  $\mathbf{c}$  director differs by  $2\pi$ , as indicated by rotation of the lens [21]. After each temperature change a pause (several minutes) sufficient to reach equilibrium of the diffraction spots positions was taken before the next measurement was performed.

The experimental results obtained for homeotropic samples are shown in Fig. 2. In the same figure the results of spectroscopic measurements using temperature scanning [22] are also shown as obtained in samples 140  $\mu\text{m}$  thick. For the calculation of  $p$  from the selective reflection band position we used the form  $p = \lambda_R/n$  assuming that in the spectral range of interest the index of refraction  $n$  is independent of temperature and wavelength. The value of refractive index  $n = 1.4$  assured consistency of data obtained from both methods. (Trying to fit the results of spectroscopic measurements to the results of the diffraction method, one must assume  $n = 1.2$  that is fairly unrealistic.)

Due to the light absorption in the investigated substances the spectroscopic measurements could be made only up to wavelength  $\lambda = 2.4$   $\mu\text{m}$ . Attempts have been made to detect the selective reflection band close to the phase transition (where the pitch, according to Fig. 1, should decrease) but no selective reflection was detected. The same behavior has been observed in 4-(2,3-epoxyhexyloxy) phenyl-4'-decyloxy

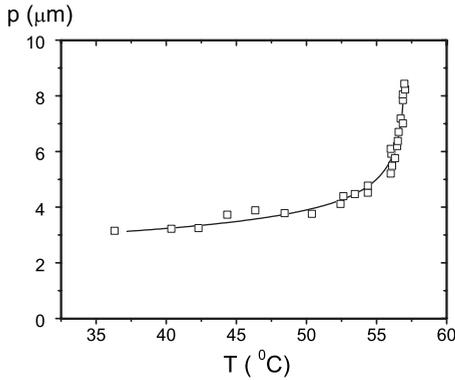


FIG. 3. The temperature dependence of the helical pitch measured in a homeotropic sample of the Epoxy compound using Cano method. Solid line below the temperature of maximum presents the best fit to the power dependence [Eq. (2)].

benzoate (Epoxy) using the Cano method (Fig. 3). In this case as well, a maximum in the  $p(T)$  dependence was observed very close to  $T_{CA}$  (0.1 K). Just before the Cano lines disappear, the helical pitch decreases as shown by diminishing of Cano-lines diameters. Above the temperature of the pitch maximum the quantitative measurements were very difficult because the Cano disclinations became irregular and were hardly visible. Because of this uncertainty the corresponding data points are not shown in Figs. 3 and 4.

As can be seen from Figs. 2 and 3, the pitch increases steadily with temperature in the whole investigated range up to very near the phase-transition point. In the vicinity of the phase transition (within about 0.1 K) the visibility of Cano lines becomes lower and the measurement uncertainty increases such that it is difficult to monitor what happens at the transition. Nevertheless, we noticed that immediately below the transition temperature the Cano lines move in the direction of the lens center. This indicates that the pitch does decrease very close to the transition (see Fig. 2).

We carried out measurements also in the commercially available material CE8. The results of helical pitch measurement obtained using spectroscopic method in homeotropic samples were already published in [23]. This experiment showed that the pitch increases monotonically with tempera-

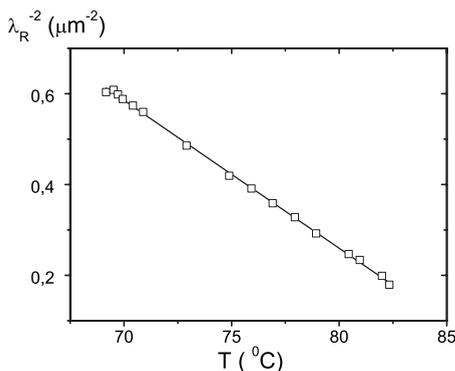


FIG. 4. Temperature dependence of the reciprocal of the square of the selective reflection wavelength of CE8 in the smectic  $C^*$  phase measured in 118- $\mu\text{m}$ -thick homeotropic sample.

ture up to 82.5  $^{\circ}\text{C}$  (i.e., 2.5 K below the transition). Above this temperature, the spectroscopic measurements cannot be performed because of strong absorption of light which wavelength exceeds 2.4  $\mu\text{m}$ . However, the observation of Cano lines performed in a sample with variable thickness demonstrated the increase in pitch with temperature up to temperatures near the phase transition  $\text{SmC}^*-\text{SmA}$  (at 85  $^{\circ}\text{C}$ ). Very close to the transition (about 0.1 K–0.2 K) the helical pitch decreases (the Cano-lines diameter get smaller, similarly as in the case of the Epoxy and C8 compounds). In the whole temperature range accessible for spectroscopic measurements, the reciprocal of the square of the selective reflection wavelength  $\lambda_R$  is, with a great accuracy, a linear function of temperature,

$$\lambda_R^{-2} = A + B \cdot T \quad (1)$$

where  $T$  is temperature and  $A=2.865 \mu\text{m}^{-2}$  and  $B=-0.032 \mu\text{m}^{-2}/\text{K}$  are constants (see Fig. 4).

### III. DISCUSSION

The comparison of data obtained for planar and homeotropic samples of C8 is shown in Fig. 2. Figure 2 demonstrates undoubtedly that the results of helical pitch measurements performed in planar and homeotropic samples differ to a large extent. We think that the distinct dissimilarity in the behavior of the pitch, especially near the phase transition, obtained for differently aligned samples can be understood as a result of surface interactions and, more specifically, as a consequence of the balance between the elastic energy of the helix and the surface anchoring energy. Usually, in diffraction experiments one tends to achieve a large anchoring energy, which is needed for a good orientation quality. In this case an orientation of molecules parallel to the glass surface is preferred. There is no internal conflict connected to this situation in the A phase. In the helical  $C^*$  phase, however, the planar boundary conditions cannot be fulfilled on the whole surface because of the presence of the tilt and of the helix. The elasticity would then tend to force the  $\mathbf{n}$  director to stay at an angle  $\alpha \approx \sin q \cdot z \cdot \sin \theta$  to the surface ( $z$  is the coordinate along the smectic layer normal). This causes an increase in the surface energy proportional to  $\sin 2\alpha$ . For small values of  $\alpha$  the elastic forces prevail. Close to the phase transition the elastic modulus is small [24,25] and the surface anchoring energy, tending to keep the molecules parallel to the substrate, can predominate. Thus, the helix will tend to brake down to allow the molecules aligning parallel to the substrate. For this reason the distance between disclination lines present in planar samples does not correspond to the bulk value of the helical pitch. The distribution of disclination lines reflects the surface properties rather than those of the helical structure. It is often the case that these lines are distributed in a very nonhomogeneous way, particularly close to the transition  $C^*-A$  [26]. This fact supports the hypothesis that the lines are simply a visualization of the nonhomogeneity in the anchoring energy. This hypothesis is strengthened by observation of broad light intensity distribution in the diffraction pattern. The observed fringes in the planar geometry are disclinations (called by Glogarova and Pavel

“dechiralization lines” [26]) and not the lines of equal extinction. This means that the distance between these “unwinding lines” may differ from the equilibrium value of the pitch. This conclusion is supported by observations made by Kondo *et al.* [7] who showed (changing the sample thickness) that the influence of the surface interactions on the apparent measured pitch values can be considerable. Thus, it seems to be proven that the surfaces influence the measured values of the pitch. The question remains as to what extent.

To answer this question attempts have to be made to diminish the surface influence as much as possible. Obviously, the surface interactions are much weaker in the homeotropic geometry (with the smectic layers parallel to the confining glass plates) than in the planar geometry, partially due to the relatively small value of the tilt angle. This supposition is supported by well-known difficulties with the orientation of the *c* director in normal, i.e., nonchiral smectics C. The conflict between surface and smectic  $C^*$  structure is not present in homeotropic samples with weak surface anchoring. The surface affects essentially only the first and the last turns of the helix neighboring the sample walls. The effect of surface forces on the internal part of the helix is rather weak. Possible effects, which could be caused by change in layers thickness, can easily be avoided by sufficiently slow temperature change. That is why the homeotropic samples represent better the bulk properties of chiral smectic C phase. Thus, the experimental results obtained in planar samples (even thick) must be treated with great care, as the systematic experimental error can be very high (see Figs. 2 and 1 in Ref. [9]). In homeotropic samples the pitch maximum is very sharp and lies much closer (0.1 K) to the transition point  $T_{CA}$  than in planar (bookshelf) samples ( $\sim 1$  K). The pitch reaches rather high values close to the transition  $SmC^*-SmA$ , comparable with the thickness of samples with planar alignment. The surface influence can thus be considerable causing erroneous results in the case of planar samples.

The correct measurement of the helical pitch  $p$  at low temperatures is quite easy; however, close to the  $C^*/A$  transition is troublesome. The main reason for this difficulty is the small value of the tilt angle  $\theta$  [27–30], which causes that electric polarizability anisotropy and, consequently, the birefringence in the smectic layer plane is small. For this reason the observation of Cano lines and registration of the selective reflection band is extremely difficult. Visual observations can be performed up to temperatures of 0.1 K below the transition  $C^*-A$ . At higher temperatures the helical structure is not observed anymore despite the nonzero value of the average molecular tilt angle. Therefore, one cannot expect that in this temperature range sufficiently accurate measurements would ever be possible which could be used for comparison with theory. In particular, it is not easy to answer the question whether the pitch decrease observed in all three investigated substances is a real bulk material property or a “finite-size” effect. The available experimental data do not allow solving of this problem.

The analysis of experimental data presented in Figs. 2–4 shows that in the whole temperature range of the  $SmC^*$ -phase (except in a region  $\sim 0.1$  K below the transition) the temperature dependence of the pitch obtained in homeotropic samples can be well described by the critical expression

TABLE I. Critical exponents for the tilt angle, spontaneous polarization and helical pitch.

Material	$\beta(\theta)$	$\beta(P_s)$	$\beta(p)$	$\beta(\theta)-\beta(P_s)$
C8	0.29	0.49	-0.25	-0.20
Epoxy	0.32	0.45 <sup>a</sup>	-0.21	-0.13
CE8	0.25	0.60	-0.50	-0.35

<sup>a</sup>Reference [27].

$$p = p_0 \left( 1 - \frac{T}{T^*} \right)^\beta. \quad (2)$$

This empirical form has actually no theoretical base; it is, however, very useful for describing various material parameters of smectic  $C^*$  liquid crystals. The critical temperature  $T^*$  is close to the phase-transition temperature  $T_{CA}$  ( $T^*-T_{CA}$  amounts to -0.1 K for C8, -0.4 K for Epoxy, and +3.3 K for CE8). It is obvious from Fig. 1 that the results of diffraction measurements on planar-oriented samples (bookshelf geometry) do not follow a similar dependence. Similar critical dependence shows other important material parameters: tilt angle  $\theta$  and the spontaneous polarization  $P_s$  [27–29]. The critical exponents for these parameters are collected in Table I.

For C8 the absolute value of the critical exponent  $\beta(p)=0.25$  is close to the critical exponent of the tilt angle ( $\beta(\theta)=0.29$ ), measured using the conoscopic technique [28].

The value of the critical exponent for the tilt angle of CE8 was inferred from our measurement of the optical activity performed in 118- $\mu$ m-thick homeotropic sample at 546 nm wavelength. The obtained temperature dependence was linear (see Fig. 5). Far from the selective reflection wavelength, the rotation of the polarization plane is approximately proportional to  $\theta^4$  [29], so in the case of linear dependence the critical exponent  $\beta(\theta)$  is about 0.25. This result agrees well with results of Raszewski *et al.* [30] and Saipa and Giesselmann [31].

### Comparison with theories

As it was demonstrated above, the majority of experimental data on the helical pitch in the smectic  $C^*$  phase suffers

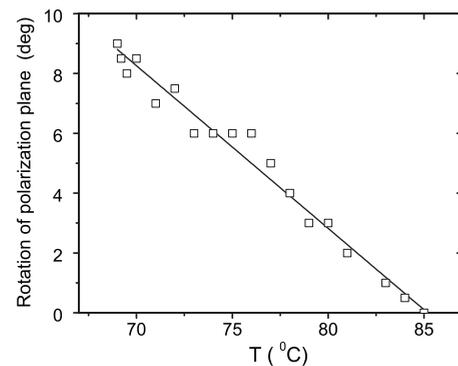


FIG. 5. Rotation of the light polarization plane (wavelength  $\lambda=546$  nm) in 118- $\mu$ m-thick sample of CE8 as function of temperature.

from an error resulting from surface interactions. It is not easy to take these interactions into account for two reasons. First, it is difficult to control the anchoring energy in experiments, especially for smectic liquid crystals. Second, it is not easy to take the anchoring energy into account in theoretical considerations without introducing many additional adjustable parameters. Probably for this reason the surface interactions are neglected in the most popular Landau-type theories [2,17,19]. Due to the lack of suitable theory, the comparison of theory and experiment can be made only for experiments in which the surface influence is small. As it was proven in the former chapter, this condition can be fulfilled in homeotropically aligned samples only. Therefore, in what follows only the results obtained for this alignment will be discussed.

One of the first attempts to describe the pitch behavior in the low-temperature range was made by Yamashita and Kimura [15]. It followed from their considerations that the helical pitch should be proportional to the  $\theta/P_S$  ratio. All three quantities,  $p$ ,  $\theta$ , and  $P_S$ , can be well approximated with critical dependencies with various exponents  $\beta$ . The values of these exponents for investigated substances are collected in the Table I. The data from the Table I do not support Yamashita and Kimura's concept. As Table I indicates, there is no agreement between the critical exponent for the pitch  $\beta(p)$  and the difference of critical exponents for tilt angle and spontaneous polarization  $\beta(\theta)-\beta(P_S)$ . The disagreement distinctly exceeds the experimental inaccuracy. Thus, the simple model by Yamashita and Kimura fails to explain the pitch behavior. Yamashita and Kimura [15] attributed the abrupt decrease in pitch close to the phase-transition smectic  $C^*$ —smectic A to the strong fluctuations of the tilt angle. The important argument against this theory was the observation made by Mušević *et al.* [32] concerning the finite value of the helical pitch at the transition. This argument is certainly true in the case of planar samples; however, in the view of observations made in homeotropic samples this argument might be doubtful—the experiment does not give any unambiguous information concerning the value of pitch at the transition point because the helix structure is smeared out there. The concept of fluctuations caused pitch reduction seems to be quite well justified when the transition has de Vries nature [33,34] and the tilt direction undergoes strong fluctuations. However, up to now accurate measurements of helical pitch in such materials have not been published.

Pikin and Osipov [35] proposed another explanation. They noticed that in the case of bent molecules the flexoelectric coefficient could have anomalous temperature dependence when the tilt angle becomes comparable with the bend angle of the molecule. Then, the helical pitch would quickly decrease close to the  $C^*$ -A transition. At low temperatures the theory predicts, in agreement with experiment, an increase in the pitch with temperature. Unfortunately, any quantitative comparison cannot be performed because the theory makes use of some molecular parameters whose values are not known.

Another explanation of the anomalous behavior of the helical pitch has been proposed by Zeks [17]. He assumed a generalized Landau expansion of the free energy of a chiral smectic  $C^*$ , taking into account biquadratic coupling of tilt and polarization. This concept was later developed in many

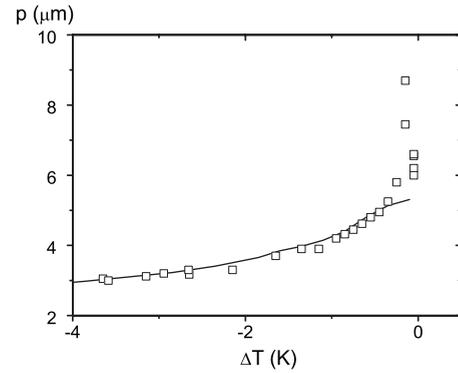


FIG. 6. Best fit of the temperature dependence of helical pitch measured in homeotropic C8 sample to the Zeks model [17] [Eq. (3)] using independently measured spontaneous polarization  $P_S$  and tilt angle  $\theta$ .

papers [e.g., [9,36,37]]. The equation for the wave vector of the helix, derived from this model, has the following form:

$$q = \frac{1}{K_3} \left( \Lambda + \mu \frac{P}{\theta} + d\theta^2 \right) \quad (3)$$

where  $K_3$  is the twist elastic constant of the  $c$  director,  $\Lambda$ —the Lifshitz constant,  $\mu$ —flexoelectric coefficient and  $d$ —a coefficient describing the coupling of the Lifshitz term with the order parameter. The above equation used for the classic ferroelectric liquid crystal DOBAMBC [2,38] described correctly the shape of  $p(T)$  dependence. However, the quantitative agreement with experimental data obtained for planar sample was rather poor.

We also attempted to apply the Zeks model [17] to our data obtained for homeotropic sample. The agreement at low temperatures (below the pitch maximum) was satisfactory. However, this theory also fails to explain quantitatively the sudden decrease above the maximum (Fig. 6). Similar results were obtained for CE8 and Epoxy samples.

Another qualitative explanation of the pitch anomaly close to the transition can be associated with the frequently observed “crossover” effect [29,31,38] of the critical exponent of the smectic C order parameter (tilt angle). This crossover takes place at temperatures 1–2 K below the transition. This is much larger temperature distance as compared with the maximum of  $p$  (0.1–0.2 K). Thus, the explanation based on the crossover effect is rather inappropriate.

As the above short review of some attempts to explain theoretically the helical pitch behavior demonstrates, none of the existing theories describes quantitatively the experimental data obtained in the proper experimental conditions. We hope our experimental results can help in search for the right theoretical model being capable of explaining the helical pitch behavior in chiral smectic C phase.

#### IV. CONCLUSIONS

The performed experiments have shown that the homeotropic orientation of the smectic  $C^*$  sample is more favorable for correct pitch measurements than the planar orientation. Due to the strong influence of surface interactions on the

helical structure in planar samples, the measurement uncertainty may significantly exceed 100%, even for relatively thick samples. The situation is better for homeotropically oriented samples, where the anchoring is weaker and does not stay in conflict with the helical structure. Only the data obtained for homeotropic aligned samples represent bulk properties of the helix. In this case, the maximum of the pitch is located very near to the smectic  $C^*$ -smectic A transition (0.1–0.2 K), much closer than in the case of planar samples (a few Kelvin). Above the temperature of maximum the helix is smeared out and, consequently, both the dielectric and optical anisotropies are extremely small and thus precise pitch measurements are impossible. For this reason only data for temperatures below temperature of maximum might be compared with theoretical predictions. The comparison of theories and experiment performed in the present paper was the first one where the bulk data were examined. Although all discussed theories correctly predict the shape of the temperature dependence of the helical pitch, none of

them provide quantitative agreement with experiment.

We suppose that the apparent decrease in the pitch with the temperature slightly below the phase transition observed in planar samples is a characteristic of the finite sample with strongly anchoring surfaces rather than of the smectic  $C^*$  liquid crystal. If so, surface interactions have to be taken into account to describe properly the properties of the system and the interpretation of numerous experimental results, based on Landau-type theory will have to be revised, perhaps by including the surface term into the free-energy expression. However, different behavior of helical structure in some other substances cannot be excluded.

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