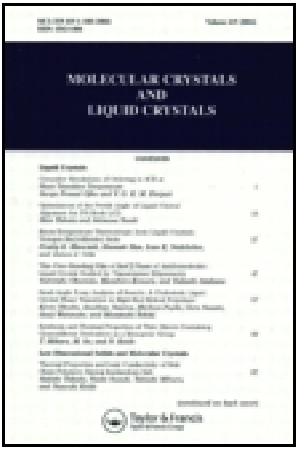

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Landau Expansion Coefficients for a Ferroelectric Liquid Crystal Showing a Polarization Sign Inversion

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To cite this article: L M. Blinov, L A. Beresnev, D. Demus, S. V. Iablonski & S. A. Pikin (1997): Landau Expansion Coefficients for a Ferroelectric Liquid Crystal Showing a Polarization Sign Inversion, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 292:1, 277-292

To link to this article: http://dx.doi.org/10.1080/10587259708031937

Mol. Cryst. Liq. Cryst., 1997, Vol. 292, pp. 277–292
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Landau Expansion Coefficients for a Ferroelectric Liquid Crystal Showing a Polarization Sign Inversion

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Capacitance, pyroelectric and electrooptical measurements have been carried out over a certain temperature range near the smectic A-C* phase transition for a Chisso compound showing the sign inversion of the spontaneous polarization with temperature. Two Landau expansion coefficients, namely, the polarization-to-tilt coupling constant C and the tilt elastic coefficient α have been calculated. Coefficient α is close to that known for conventional ferroelectric liquid crystals (e.g., DOBAMBC), coefficient C manifests nonmonotonic temperature dependence with a maximum well above the A-C* transition and an inflection point at the transition. This behaviour may qualitatively be understood if the biaxiality induced by a molecular tilt is taken into account.

Keywords: Ferroelectricity; phase transitions; spontaneous polarization; smectics

1. INTRODUCTION

The present paper deals with ferroelectric liquid crystals, the field of rather recent interests of Prof. A. Saupe. Nevertheless, Alfred's contribution to this area is also very significant; it is sufficient to mention his fundamental description of elastic distortions in the smectic C phase [1], and explanation of the nature of electromechanical effects in chiral ferro [2] and antifer-

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roelectric [3] phases. Electromechanical effects are tightly related to the field induced changes of the tilt angle (the electroclinic effect [4]) discussed in the present paper for a particular case of a ferroelectric liquid crystal with temperature inversion of the sign of spontaneous polarization P_s.

In ferroelectric liquid crystals, at the transition from the smectic A into the chiral smectic C* phase, the spontaneous polarization appears as a secondary order parameter simultaneously with tilt angle ϑ of the longitudinal molecular axes with respect to smectic layers. In most of the cases, P_s is proportional to ϑ over a rather wide temperature range of the C* phase, as it also follows from the simplest Landau description with temperature independent polarization-tilt coupling constant (piezocoefficient) C [5, 6].

However, in some substances a strong deviation from the linear P_s (ϑ) dependence is observed. Moreover, the inversion of sign of the spontaneous polarization (P_s) at a certain temperature in the smectic C* phase is being repeatedly reported. This phenomenon seems to be very intriguing. Up to now it has been observed in two systems: (i) in single component substances whose molecules have very flexible tails with at least one CH_2 chain between a chiral center and a rigid molecular core [7–14] and (ii) in two-component mixtures with rather rigid molecules [15].

The inversion phenomenon has been interpreted in terms of three models. For flexible molecules mentioned above a competition between chiral tail isomers with different direction of the molecular dipole moment is usually considered. These isomers contribute to spontaneous polarization with opposite signs. The concentration of the two isomers is changing with temperature and, at a certain temperature point, P_s changes sign [8, 9].

Another interpretation is based phenomenologically on the extended Landau model suggested by Zeks (see, e.g., Chapter 5 in [6]) where a non-chiral biquadratic coupling between the tilt and polarization is taken into account. Microscopically this coupling originates from the quadrupolar ordering of transverse molecular axes in the tilted phase [16, 17]. When a molecule has a special shape [18, 19] (lath-like form, with a steric and electric dipoles having different directions) the competition arises between the polar and quadrupolar ordering. The azimuthal orientational order for the steric dipole is proportional to the tilt angle, while the molecular quadrupole is oriented proportionally to the tilt squared. With a molecular electric dipole fixed at a certain angle with respect, say, to the steric one, the competition may result in two possible directions of the electric dipole with respect to the plane of molecular tilt, that is, in the polarization sign inversion at a certain temperature. This theoretical approach has been used for interpretation of the P_s inversion phenomenon in [13, 19, 20].

The third explanation is related to mixtures of chiral guests and achiral hosts [15]. In a mixture, the guest-guest and guest-host parts of the interaction energy are considered to be differently dependent on the order parameter (tilt angle) of the C* phase. Thus, the P_s sign inversion is possible with a change in both the guest concentration and temperature.

Typical values of the spontaneous polarization measured in the range between the smectic A-C* transition and the inversion point (5–10°C) are rather small, 1–10nC/cm^2 or even less [15]. That is why it is rather difficult to make precise measurements of the tilt angle and especially polarization near the A-C* transition by a conventional switching techique. Therefore, in order to evaluate Landau expansion coefficients one should use another, more sophisticated technique.

The aim of the present work was to carry out capacitance, pyroelectric and electrooptical measurements over a certain temperature range near the smectic A-C* phase transition for a Chisso compound studied earlier [13] and to calculate two Landau expansion coefficients, namely, the polarization-tilt coupling constant C and the tilt elastic coefficient α. These coefficients are compared with C and α values for conventional ferroelectric liquid crystals (such as classical DOBAMBC) in order to shed light on applicability of the Landau theory to materials with polarization inversion.

2. LANDAU DESCRIPTION

In framework of the simplest Landau model, Refs. 2 and 3 (Chapter 5), for a ferroelectric liquid crystal, the free energy taken in the SI unit system is:

$$g = \frac{1}{2}a_0\vartheta^2 + \frac{1}{4}\beta\vartheta^4 + \frac{P^2}{2\varepsilon_0\chi_1} - CP\vartheta - PE + \text{chira 1 terms} \qquad (1)$$

where ϑ [in rad] is the tilt of the director, $a_0 = \alpha(T - T_0)$ [in J/m^{3}K] describes the elasticity for $\delta\vartheta$ changes, P[in C/m^2] is polarization, C[in V/m] is the $P - \vartheta$ coupling constant (or piezocoefficient μ_p in [1]), E is an external electric field, $\chi_\perp = \varepsilon_\perp - 1$ is the background relative dielectric susceptibility that may be taken from the isotropic phase, ε_0 [in F/m] is the dielectric constant of vacuum. Chiral terms are rather complex and only important for a helical ferroelectric. During the tilt, polarization and susceptibility measurements on thin cells the helical structure is assumed to be unwound and all chiral terms are disregarded.

Let us discuss the behaviour of the system near the A-C* transition and in the smectic A phase. In this case, with an exception of very strong fields we can assume small ϑ angles and a linear relationship between the additional polarization (over the background value $\chi_\perp E$) and tilt

$$P=\chi_\perp \varepsilon_0 C \vartheta \tag{2}$$

Then, after minimization with respect to the tilt angle we arrive at the Curie-Weiss type expression for the linear in field electroclinic tilt angle:

$$\vartheta = e_c E = \frac{\chi_\perp \varepsilon_0 C E}{a_0 - \chi_\perp \varepsilon_0 C^2} = \frac{\chi_\perp \varepsilon_0 C E}{\alpha_0 (T - T_c)} \tag{3}$$

with

$$T_c = T_0 + \frac{\chi_\perp \varepsilon_0 C^2}{\alpha} \tag{4}$$

Here, e_c is so-called electroclinic coefficient. If the helical structure is unwound a growth of the induced tilt at the phase transition is limited by $\beta\vartheta^4/4$ term in expansion (1).

Combining Eqns. (2) and (3) we have an expression for the low field soft-mode susceptibility in the smectic A phase or for the field induced polarization P:

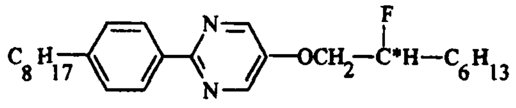
$$\chi_{sm} = \frac{P}{\varepsilon_0 E} = \frac{\chi_\perp^2 \varepsilon_0 C^2}{\alpha (T - T_c)} \tag{5}$$

If temperaure dependences of the field induced tilt angle (3) and polarization (or soft mode susceptibility) (5) are measured, two unknown Landau expansion coefficients α and C may be calculated. In the spirit of the Landau theory both quantities are assumed to be independent of temperature. However, in substances with spontaneous polarization sign inversion the spontaneous tilt angle (for example measured by the X-ray technique [13]) monotonously increases with decreasing temperaure. Thus we can anticipate a specific temperature dependence of the polarization-to-tilt constant and, perhaps, a temperature dependent coefficient α.

3. EXPERIMENTAL

3.1. Substance and Cells

For our experiments, there was chosen a Chisso phenylpyrimidine derivative (8PPy06)



with phase sequence

$$\mathrm{Cr{-}46.2^{\circ}C{-}(S_X^*{-}25^{\circ}C{-}S_c^*{-}45^{\circ}C){-}S_A{-}80^{\circ}C{-}Iso},$$

$P_s = 27\mathrm{nC/cm^2}$ at $T = 30^{\circ}\mathrm{C}$ and polarization sign inversion point $T_i = 37.7^{\circ}\mathrm{C}$ measured in [13] by repolarization current technique.

The samples were prepared as follows. Two ITO covered glass plates were separated with 8μm thick teflon spacers and filled with a liquid crystal in the isotropic phase. One of the ITO electrodes was covered with a polyvinylalcohol layer and rubbed unidirectionally. The absence of any diffraction on the helical pitch indicates that we deals with unwound helix. A d.c. electric voltage varied from 0 to 30V could be applied in series with a load resistor to the same electrodes. The area overlapped by electrodes was $A = 11.5\mathrm{mm}^2$. We also used a cell with one ITO glass plate covered by SiO layer evaporated obliquely and the other covered by a surfactant and had qualitatively the same results.

3.2. Measurements

For all of measurements we used a simple set-up based on a lock-in technique. The cells were kept in a thermal jacket with temperature controlled by a thermocouple with amplification of its thermo-e.m.f. by a d.c amplifier. The thermocouple was placed between two glasses in a symmetrical position with respect to the liquid crystal cell. The temperature was measured by a digital multimeter (Model Voltcraft M4650CR) with accuracy of 0.01°C. The output of the multimeter was connected to IBM-PC computer.

The thermal jacket was installed on a polarizing microscope which allowed the observation of the texture and the installation of a Si photodiode or a laser diode instead of a microscope ocular. Thus electrooptical, pyroelectric and capacitance measurements can be a carried out exactly in the same regime on sample cooling.

For measurements of the capacitance and electrooptical response, a cell was connected in series to a function generator Philips PM5138 (and a dc voltage source when necessary) and to a load resistor from which an electric signal was delivered to a lock-in amplifier, PAR 5210, synchronized by the same function generator. For electrooptical measurements a signal from photodiode was measured by the same lock-in amplifier.

a) Tilt angle measurements

In fact, we measured field induced optical transmission of a cell placed between crossed polarizers and oriented at an angle $\varphi = 10°$ with respect to a polarizer. The square wave electric voltage (0.1–10V) at frequency 3Hz rotates the optical axis of a cell in its own plane around angle φ through small angles $\delta\varphi$ not exceeding 7–8 deg. In this case, according to the Malus law, $I \propto I_0 \sin^2 2(\varphi + \delta\varphi)$, the transmission is a linear function of angle $\delta\varphi$ as long as $4\delta\varphi$ is less than 1 and may be recorded automatically by the computer as a function of temperature without rotation of a microscope table. In fact, even for $\delta\varphi = 8°$ the error in the angle measurements does not exceed 10%. The absolute calibration was made by conventional technique described earlier [21]. It is based on observation of an oscillogram of the electrooptical response of the same cell. By rotating a cell with a microscope table and proper minimization of the response for a positive and negative parts of a square wave voltage (frequency is 350 Hz) we can measure 2ϑ angle for certain voltages and then fit all of the transmission curves.

b) Polarization measurements

For the measurements of polarization the pyroelectric technique has been used. This technique is easily computerized and very convenient for cumbersome measurements of the $P(T)$ dependences at various fields.

The total pyroelectric coefficient is the first derivative of the total polarization with respect to temperature:

$$\gamma = \gamma_s + \gamma_i = \frac{d(P_s + P_i)}{dT} \tag{6}$$

Here, the induced polarization is

$$P_i = \varepsilon_0 \chi E = \varepsilon_o E(\chi_\perp + \chi_{sm} + \chi_G) \tag{7}$$

where the total material susceptibility includes the background dielectric susceptibility, soft mode susceptibility related to the field induced change in the tilt angle, and the Goldstone mode related to a change in the azimuthal angle of the director in the C* phase. Each of the terms has its own characteristic temperature dependence which can be easily extracted from the total pyroelectric response.

In experiment, a beam of a 30mW laser diode ($\lambda = 690$nm) was used to provide a small local temperature change ΔT in a sample due to partial absorbance of light in glasses and ITO layers. The light was chopped at frequency $\omega = 7$kHz by square pulses from the TTL output of the function generator and directed onto a FLC cell through the microscope. The periodic modulation of sample temperature causes a change in the polarization ΔP and, consequently, a change in the surface density of charge $\Delta\sigma$ across cell electrodes.

The pyroelectric response was measured as a two component (X and Y) sine voltage across the load resistor R = 10MOhm with the same lock-in amplifier and computer. A d.c. voltage varied from -10 to $+10$V may be applied to the cell. The temperature dependence of the polarization (on an arbitary scale) was calculated by integrating the pyroelectric voltage starting from a temperature well above the A-C* transition. Then the correct scale for P was introduced by fitting P at several temperatures to the values measured independently with the standard repolarization current technique (square- wave pulses with 20Vp-p voltage and repetition rate of 300Hz were applied to a cell).

(c) Soft mode susceptibility measurements

The soft mode dielectric susceptibility can be calculated from the temperature dependence of the capacitance component of the a.c. current through the cell, measured as a voltage across a load resistor of 2kOhm (at frequency 300Hz) by the same lock-in amplifier. This technique is very convenient as it allows for the automatic measurements of the soft mode susceptibility peak just under the microscope, in the same thermal regime of the cell.

4. EXPERIMENTAL RESULTS

Figure 1 shows dielectric permittivity of a 8 μm cell measured with very low a.c. electric voltage either without a d.c. bias or with $U_{dc} = 1\,V$. The peak of the soft mode susceptibility, not reported earlier for substances with P_s inversion, is clearly seen. In addition, a deep minimum near 37–38°C points to the polarization sign inversion temperature T_i. Application of the bias voltage, as expected, supresses the soft mode peak. We believe that the soft mode peak position corresponds to the zero-field A-C* transition point, $T_c = 45.1$°C.

Figure 2 shows the apparent tilt angle as a function of temperature for two amplitudes of the square wave voltage. The apparent tilt was measured as the electrooptical (transmission) response, normalized at $T = 43$°C to the tilt angle $\delta\varphi = \theta_{app} = 8°$ found by the table rotation technique. The, two curves show the polarization sign inversion precisely at the same temperature $T_i = 37.75$°C. On both sides of the inversion point the absolute value of

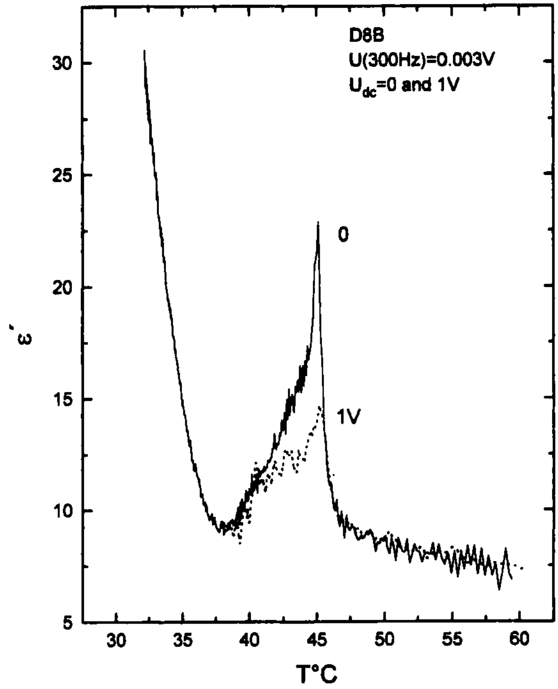


FIGURE 1 Dielectric permittivity of PPy8.06 measured at a.c. voltage $U = 0.003\,V$ (300Hz) without bias and with a d.c. voltage of 1V.

the apparent tilt angle for $U = 10V$ is almost the same (about 0.17 rad or 10°) and close to the value of the optical tilt ($\approx 12°$) reported earlier for much higher field [13]. It means that we have almost complete switching at ±10V. In the smectic A phase, a typical "tail" of the electroclinic response is observed.

Figure 3 displays the temperature behaviour of the pyroelectric coefficient (above) and total polarization (below) measured on the same cell either at zero bias or at a d.c. voltage of $+10V$ applied. Curve $\gamma(T)$ for zero field has one zero point and , after integrating, spontaneous polarization P_s (below) shows sign inversion at 39.8°C. For bias voltage of $10V$ the pyroelectric curve shows two zero points. The second one corresponds to the sign inversion point because here a strong field reorients the polarization and changes sign of the pyroresponse. The new location of T_i coincides with that determined from electrooptical measurements. The curve for P at $10V$ does not cross abcissae just for the reason mentioned: both below and above the inversion point polarization is directed along the external field irrespectively

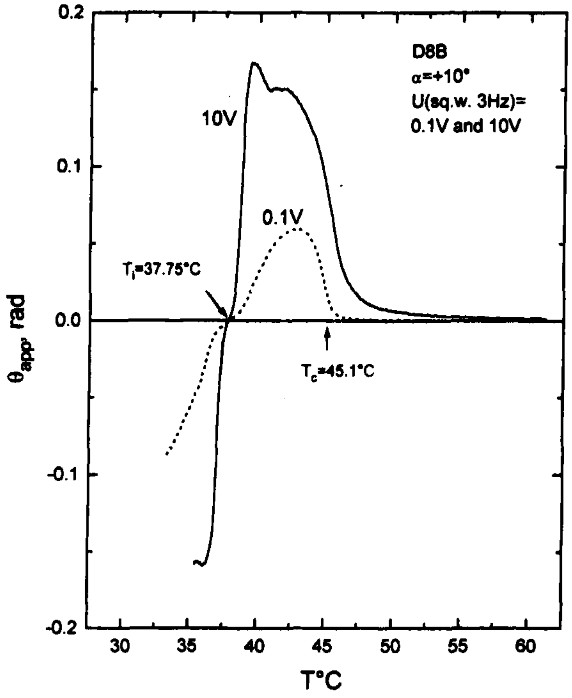


FIGURE 2 Apparant field induced tilt angle measured with a square wave voltage of $\pm 0.1V$ and $\pm 10V$ at frequency 3Hz.

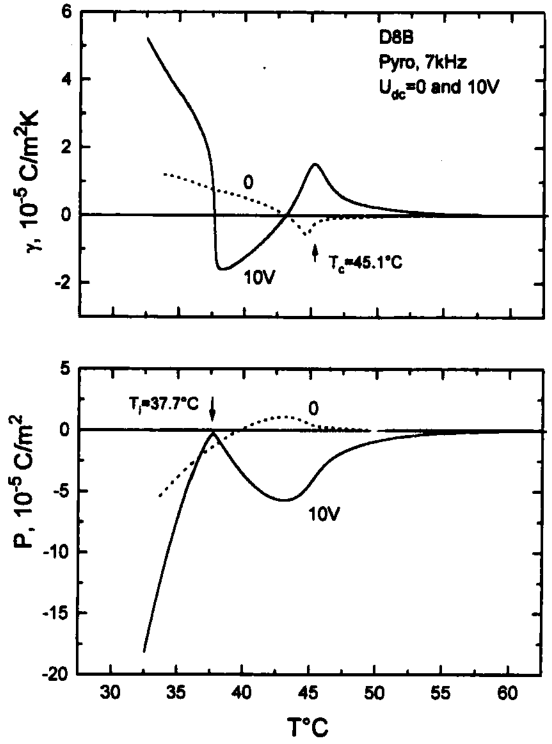


FIGURE 3 The temperature behaviour of the total pyroelectric coefficient γ (above) and total polarization P (below) measured at frequency 7kHz either without bias or with a d.c. voltage of $+10V$ applied to the cell electrodes.

of its sign. In the smectic A phase, a typical "tail" of the field induced polarization anticipated from Eqn. (5) is observed.

Now, we would like to make a comment concerning the zero-field curve for polarization measured by the pyroelectric effect. When the pyroeffect was measured at rather high frequency of 7kHz we observed sign inversion of P_s for all our cells, including even old ones filled with the substance doped with TCNQ. This is in contradiction with the statement made by us at the Cambridge conference [22]. Earlier we made measurements at 70Hz and could not separate the true pyroelectric effect from the thermal modulation of the space charge double layers adjacent to electrodes. These layers may manifest themselves also in the smectic *A* or isotropic phase and, after application of a voltage to a cell, even provide an external long living zero-field current originated from the polarization of electrodes. Certainly such layers may influence the polarization measurements by a switching technique as well. Probably, this effect is also responsible for the difference in T_i points at zero and finite bias voltage, Figure 3 (below). The pyroelectric effect seems to be a powerful tool for a study of such phenomena.

5. DISCUSSION

As we have seen, qualitative behaviour of susceptibility, field induced polarization and electroclinic effect is consistent with what is expected from the Landau description. Let us try to estimate the most important Landau coefficients C and α. To avoid the integration procedure which may reduce accuracy, we can present the pyroelectric coefficient from Eqns. (5) and (7) as follows:

$$\gamma = \frac{dP}{dT} = -\frac{\chi_{\perp}^2 \varepsilon_0^2 C^2 E}{\alpha (T - T_c)^2} \tag{8}$$

Thus, using Eqn. (3), we should have a temperature independent apparent coefficient α_{app}:

$$\alpha_{\text{app}} = \frac{\gamma(T) E}{\vartheta^2(T)} \tag{9}$$

The result of such a calculation is shown in Figure 4. The apparent α-coefficient strongly depends on temperature. Even in the smectic A phase it changes within one order of magnitude. Thus, strictly speaking the Landau description (1) is not valid. We can, however, proceed further on and verify a validity of the Curie-Weiss law separately for the tilt angle and induced polarization, Eqns. (5) and (7).

Figure 5 displays the reciprocals of both the induced tilt angle and polarization as functions of temperature. The behaviour of the two curves is quite different; the inverse tilt does obey the Curie-Weiss law within a range of 2–6°C from the A-C* transition, the inverse polarization does not. Thus, a deviation from the Landau-type behaviour has mostly to be attributed to the temperature dependence of the induced polarization (or field dependent susceptibility). Indeed, a field dependence of the soft-mode susceptibility is seen in Figure 1.

It is of interest to calculate from Eqn. (2) the apparent polarization-to-tilt ratio. As expected, the product $\varepsilon_0 \chi_{\perp} C$ depends on temperature, Figure 6. It

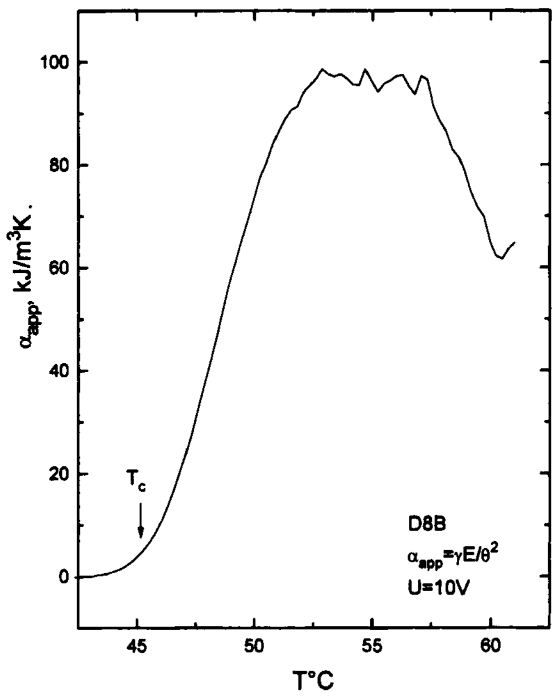


FIGURE 4 Apparent Landau coefficient α calculated from Eqn. (12). γ and ϑ measurements were carried out at $U = 10V$

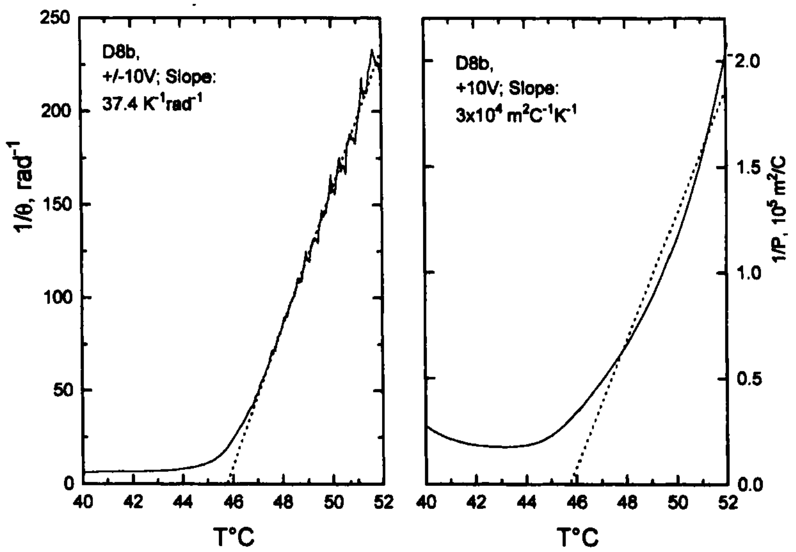


FIGURE 5 Attempts at fitting of the reciprocal tilt angle (left) and reciprocal polarization (right) in the smectic A phase to the Curie-Weiss law.

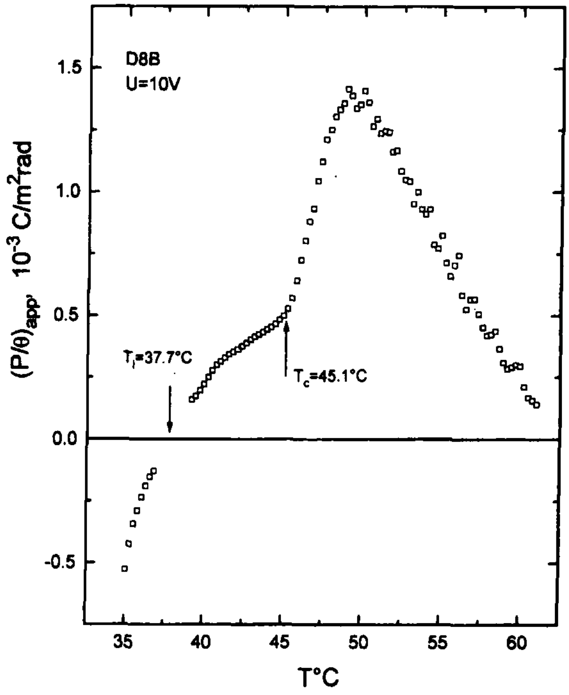


FIGURE 6 Apparent polarization-to-tilt ratio (at $U = 10$V) as a function of temperature.

has a maximum well above the A-C* transition, at $T - T_c \approx 5$°C. We can use the average value of $P/\vartheta \approx 1.25.10^{-3}$ C/m^2 rad in the range $T - T_c \approx 2$–6°C (where Curie-Weiss law is fulfilled for the inverse tilt) and estimate Landau coefficient $\alpha \approx 59$kJ/m^{3}K from the $\vartheta^{-1}(T)$ slope, Figure 5 (left). To have the same α in the same temperature range, the inverse polarization has to have a slope shown by the dotted line in Figure 5 (right). It is seen that such an approximation is far from the real curve.

With the same P/ϑ ratio, the α-coefficient may also be estimated from the zero field susceptibility shown in Figure 1:$\alpha \approx 53$kJ/m^{3}K, very close to the value found from the tilt angle. This value is also close to that for a classical compound DOBAMBC and other substances [23].

The polarization-to-tilt ratio shows a certain anomaly (an inflection point) just at the phase transition. Such an anomaly has also been observed in experiment on ferroelectric mixtures showing no inversion phenomena [23].

Both the maximum of C in the A phase and the inflection point at the transition may be understood in framework of the theory[20] that takes the tilt induced biaxiality into account (no matter the spontaneous or the field induced tilt is considered). It has been shown that the polarization may be expressed explicity in terms of tilt angle ϑ and biaxial order parameter B:

$$\frac{P}{\vartheta} \propto (1 + B) \tag{10}$$

where $B \propto \vartheta^2$ only at very small tilt angles, $\vartheta < 10^{-2}$. With decreasing temperature (in the smectic C* phase) parameter B manifests a nonlinear dependence on temperature. The polarization sign inversion effect may be described phenomenologically by incorporation of factor $[1 + K(T - T_c)]B$ instead of B in Eqn. (10), constant K being positive:

$$\frac{P}{\vartheta} \propto \{1 + [1 + K(T - T_c)]B\} \tag{11}$$

Eqn. (11) describes qualitatively the observed temeperature behaviour of the polarization-tilt coupling constant, Figure 6. Indeed, far from T_c, $T > T_c$, we have $B(T - T_c) \propto E^2/(T - T_c)$, that is P/ϑ increases with decreasing temperature. In close proximity to T_c in the A phase, $B(T - T_c) \propto E^{2/3}(T - T_c)$, that is P/ϑ has a maximum. Then, on approaching T_c it decreases. In the C* phase, in close proximity to T_c, the magnitude of $[1 + K\ (T - T_c)]B$ contains an additional positive term, proportional to $(T - T_c)$ an related to the finite spontaneous tilt angle $\vartheta_0 \propto (T_c - T)^{1/2}$, therefore in the C* phase, the P/ϑ temperature dependence has a smaller slope. Far from T_c, at $T < T_c$, P/ϑ changes sign and, after this, manifests a much steeper temperature dependence controlled by a nonlinear $B(\vartheta)$ function.

Thus, the nonmonotonic behaviour of the polarization-tilt coupling constant may be accounted for in terms of the model [20]. On the other hand, we cannot exclude a possibility of another explanation of our results, based, for example, on consideration of various molecular conformers although for this particular substance the very existence of such conformers is not evident.

6. CONCLUSION

Thus, we conclude that in PPy8.06 the soft-mode susceptibility, field induced tilt angle and polarization may be qualitatively understood in framework of the simplest Landau approach. However, the Landau expansion coefficients (polarization-to-tilt ratio and tilt elastic modulus) appear to be strongly temperature dependent. Especially interesting is different temperature behaviour of the field induced tilt angle and polarization in the smectic A phase (even far from the phase transition and at relatively low fields). The former obeys the Curie-Weiss law, the latter does not. Therefore, a modification of the simplest Landau approach is necessary. It has been shown that the observed temperature behaviour of the Landau expansion coefficients may be understood if biaxiality induced by the molecular tilt (either spontaneous or field induced) is taken into account.

Acknowledgements

The authors are grateful to Dr. S. Saito and Dr. T. Inukai (Chisso) for supplying 8PPy06 sample. The help of Mr. S. G. Kononov, Dr. K. Saxena and Dr. D. Subachius is also acknowledged. The work was partly supported by Russian Fund for Basic Researches (grant 95-02-03541).

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