

## Mean-field coefficients and the electroclinic effect of a ferroelectric liquid crystal

F. Gießelmann and P. Zugenmaier

*Institute of Physical Chemistry, Technical University Clausthal, D-38678 Clausthal-Zellerfeld, Germany*

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Experimental data on the temperature and electric field dependence of the tilt angle and the electroclinic effect of the smectic- $C^*$  (Sm- $C^*$ ) and the smectic- $A^*$  (Sm- $A^*$ ) phases are presented which have been obtained by electrooptical investigations on the ferroelectric liquid crystal mixture FLC 6430 from Hoffmann-La Roche, Basle, Switzerland. The data are analyzed according to the generalized Landau expansion and the results of a microscopic model for spontaneous polarization. The mean-field coefficients obtained from a fit of the Landau approach to the experimental data are discussed with respect to the electroclinic effect, the specific heat singularity, and the chirality. The results support the evidence of quadrupolar ordering and biquadratic coupling for the description of the Sm- $C^*$ -Sm- $A^*$  phase transition. The Landau model is extended to temperatures far below the phase transition.

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### I. INTRODUCTION

In 1975 Meyer *et al.* [1] established the existence of a spontaneous polarization and a helical superstructure of the chiral smectic- $C$  phase (Sm- $C^*$ ) of (*S*)-*p*-(*n*-decyloxybenzylidene)-*p*-amino-(2-methylbutyl)cinnamate (DOBAMBC). Five years later Clark and Lagerwall [2] demonstrated the (improper) ferroelectricity of the Sm- $C^*$  phase in thin surface stabilized cells and found submicrosecond and bistable switching properties. Since that date, the experimental and theoretical study of ferroelectric liquid crystal physics has attracted considerable efforts, leading to a rapidly growing field of liquid crystal research. Recently, a comprehensive review on ferroelectric liquid crystals was published [3].

Numerous experimental work focuses on the unique optical and electrical properties of the Sm- $C^*$  phase and its switching dynamics in external fields. Actually, little is known about the basic thermodynamic functions of the Sm- $C^*$  phase and the Sm- $C^*$ -smectic- $A$  (Sm- $A^*$ ) phase transition, respectively. A phenomenological description of static and dynamic Sm- $C^*$  properties is based on a Landau-type expansion of the free energy at the Sm- $C^*$ -Sm- $A^*$  phase transition [4,5]. In 1983 a molecular statistical theory of ferroelectric liquid crystals was presented by Osipov and Pikin [6], which was also discussed by Urbanc and Žekš [7] in 1989.

In order to correlate experimental results and theoretical description or to investigate the structure-property relationship of ferroelectric liquid crystals, it is essential to determine the Landau-expansion coefficients from experimental data. Those coefficients that are chiral in character and related to the coupling of the tilt angle and the polarization may conveniently be determined by investigations on the temperature and tilt angle dependence of the spontaneous polarization or by investigations on the dielectric dispersion of ferroelectric liquid crystals. But only a few attempts had been made to determine the absolute values of the nonchiral coefficients  $\alpha$ ,  $b$ , and  $c$  of the Landau expansion [cf. Eq. (1)]. Their contribution to

the total free energy density is much larger than those from the chiral ones and therefore,  $\alpha$ ,  $b$ , and  $c$  predominantly govern the tilt angle and the thermodynamic properties of the nonchiral Sm- $C$  as well as the chiral Sm- $C^*$  phase.

In principal, the nonchiral coefficients  $\alpha$ ,  $b$ , and  $c$  can be obtained by an analysis of heat capacity measurements. In 1983 Carlsson and Dahl [8] determined the values for DOBAMBC by differential scanning calorimetry and in 1986 Dumrongrattana, Huang *et al.* [9,10] investigated the values for DOBAMBC again by high-resolution ac calorimetry. Obviously, a determination of  $\alpha$ ,  $b$ , and  $c$  by calorimetric methods seems to be rather difficult and needs highly sophisticated experimental techniques due to the small calorimetric response of the continuous second order Sm- $C^*$ -Sm- $A^*$  transition and the considerable influence of smearing effects [11]. Therefore, the values reported by Carlsson and Dahl differ by orders of magnitude from the ones reported by Dumrongrattana, Huang *et al.* for the same compound (cf. Table I).

In the case of a chiral Sm- $C^*$ -Sm- $A^*$  phase transition, another possibility for a determination of  $\alpha$ ,  $b$ , and  $c$  may be considered by analysis of the electroclinic effect of the Sm- $A^*$  [Fig. 1(a)] and the Sm- $C^*$  phase [Fig. 1(b)]. The electroclinic effect of chiral smectic phases was found by Garoff and Meyer [12] in 1977. The linear electroclinic response of the Sm- $A^*$  phase to an electric field is closely related to the harmonic  $\alpha(T - T_c)\Theta^2/2$  term of the Landau expansion [cf. Eq. (2)] and has been widely investigated [3,13,14]. But if  $T$  approaches  $T_c$ , the harmonic term vanishes and the inharmonic higher order  $b$  and  $c$  terms determine the size and nonlinearity of the electroclinic effect. As shown in this paper, a measurement and numerical analysis of the electroclinic effect in the vicinity of the Sm- $C^*$ -Sm- $A^*$  phase transition provides a powerful method for a determination of the nonchiral Landau coefficients  $\alpha$ ,  $b$ , and  $c$ .

To our knowledge, the first estimation of  $\alpha$ ,  $b$ , and  $c$  from the electroclinic effect was given by Bahr, Heppke,

TABLE I. Summary of values for coefficients of Landau expansions.

Authors [Ref.]	Compound	$\alpha$ (kJ m <sup>-3</sup> K <sup>-1</sup> )	$b$ (kJ m <sup>-3</sup> )	$c$ (kJ m <sup>-3</sup> )	$A_1$ (C K m <sup>-2</sup> )	$A_2$ (K)	$C$ (V m <sup>-1</sup> )	$\Omega$ (V m C <sup>-1</sup> )	$\chi_{0,r}$	$T_c$ (K)
This work	FLC 6430	26.5	66.9	8 010	0.322	542	$12.9 \times 10^{6d}$	$22 \times 10^{9e}$	8.4	330.45
Carlsson and Dahl [8]	DOBAMBC <sup>a</sup>	50	85	14 000			$1.3 \times 10^{6f}$	g	9	367.3
Huang and co-workers [9,10] <sup>b</sup>	DOBAMBC <sup>a</sup>	22.6	260	4 500			$2.8 \times 10^6$	$570 \times 10^9$	2.6	367.3
Bahr, Heppke, and Sabaschus [14]	<i>L</i> -7 <sup>c</sup>	89	-85	8 800			$85 \times 10^6$	g	4	345.5

<sup>a</sup>DOBAMBC is (S)-*p*-(*n*-decyloxybenzylidene)-*p*-amino-(2-methylbutyl)cinnamate.

<sup>b</sup>Values for  $T_c - T = 5$  K.

<sup>c</sup>*L*-7 is (*L*)-4-(3-methyl-2-chlorobutanoyl-oxy)-4'-heptyloxybiphenyl.

<sup>d</sup>Calculated from  $A_1$  by Eq. (9a) for  $T = 298$  K.

<sup>e</sup>Calculated from  $A_2$  by Eq. (9b) for  $T = 298$  K.

<sup>f</sup>Calculated by  $P_0 = \chi_0 C$  [cf. Eq. (6)] with  $P_0 = 10^{-4}$  C m<sup>-2</sup>.

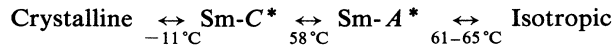
<sup>g</sup>Classical Landau expansion without biquadratic coupling term.

and Sabaschus [14] in 1988 for a first order Sm-*C*\*–Sm-*A*\* phase transition. Based on the classical Landau model, they obtained  $a$  from the linear electroclinic response of the Sm-*A*\* phase and fitted  $b$  and  $c$  from the temperature dependence of the Sm-*C*\* tilt at zero electric field. In this paper, the (nonlinear) electroclinic response of the Sm-*A*\* and the Sm-*C*\* phase is considered and evaluated in terms of the generalized Landau model.

After reporting the experimental procedures for data collection (Sec. II), we briefly discuss the generalized Landau model in Sec. III. An expression that is suitable for an evaluation of the experimental results is derived in Sec. IV by introducing some results of a microscopic model for the spontaneous polarization into the generalized Landau expansion. In the following section the chiral coupling coefficients are derived from the tilt angle dependence of the spontaneous polarization. The field- and temperature-dependent tilt angle data are presented in Sec. VI. The coefficients  $\alpha$ ,  $b$ , and  $c$  are determined from these data and compared to literature. The results are discussed with respect to the electroclinic effect (Sec. VII), thermodynamic functions (Sec. VIII), and chirality (Sec. IX). Finally, the Landau model is extended to temperatures far below  $T_c$ .

## II. EXPERIMENTAL

The ferroelectric liquid crystal (LC) mixture “FLC 6430” from Hoffmann–La Roche, Basle, Switzerland, was investigated, which exhibits a broad Sm-*C*\* temperature range and high spontaneous polarization. The phase sequence of FLC 6430 according to literature data is



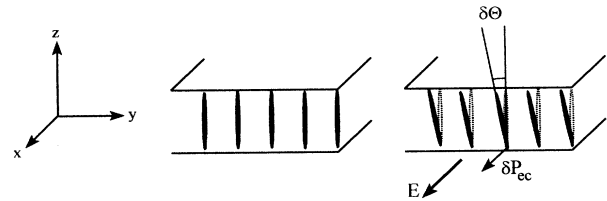
FLC 6430 exhibits a broad two-phase region, Sm-*A*\* and isotropic, between 61 and 65°C.

The mixture FLC 6430 was filled by capillarity into 4- $\mu$ m cells from E.H.C. Co., Tokyo, with transparent electrodes (ITO) and coated with an antiparallel rubbed polyimide alignment layer. The formation of a striped bookshelf texture, which is well known for FLC 6430 [15], was avoided by rapidly cooling the sample from the Sm-*A*\* phase to 25°C and orienting the sample by a high electric ac field with 5-V/ $\mu$ m amplitude. After this procedure a well oriented bookshelf configuration was

achieved.

With regard to the electroclinic effect, it is necessary to measure precisely the director tilt angle as a function of temperature and electric field strength. An ac electric field has to be applied in order to avoid a screening of the external field by ionic impurities [16]. Tilt angle measurements were carried out electro-optically by the method proposed by Bahr and Heppke [17]. This method is briefly described in Fig. 2 and provides the apparent tilt angle, which matches the director tilt angle if

a) Sm*A*\* phase:



b) Sm*C*\* phase:

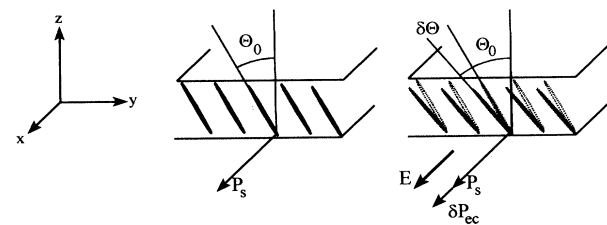


FIG. 1. Electroclinic effect of the Sm-*A*\* (a) and the Sm-*C*\* (b) phase. (a) At zero electric field conditions, the molecules of a Sm-*A*\* phase are oriented parallel to the smectic layer normal ( $z$  direction). An electric field  $E$ , which is directed parallel to the smectic layer plane [ $(x, y)$  plane] induces an electroclinic polarization  $\delta P_{ec}$  and inclines the molecular orientation by a tilt angle  $\delta\theta$ . The tilt direction is perpendicular to the electric field. (b) At zero electric field conditions, the molecules of a Sm-*C*\* phase are spontaneously tilted with respect to the layer normal by a tilt angle  $\theta_0$ . The spontaneous polarization of the Sm-*C*\* phase  $P_s$  is directed perpendicular to the tilt plane [ $(y, z)$  plane]. An electric field  $E$ , which is applied perpendicular to the tilt plane and parallel to  $P_s$ , induces an electroclinic polarization  $\delta P_{ec}$  parallel to  $P_s$  and an additional tilt angle  $\delta\theta$ .

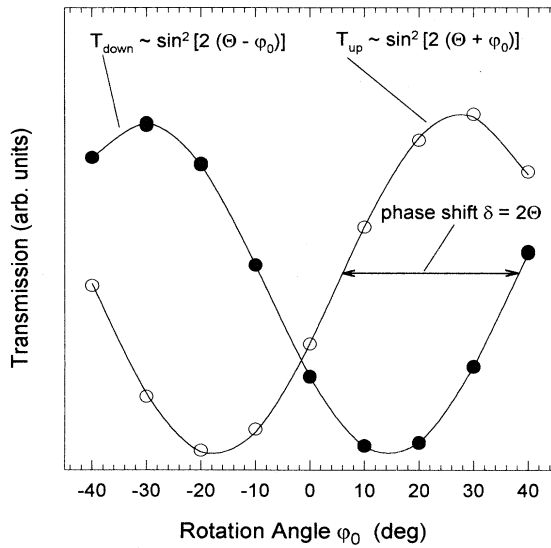


FIG. 2. Determination of director tilt angles  $\Theta$  by electro-optical measurements (see Ref. [16]). The FLC sample is switched in a bookshelf configuration by an ac-electric square field. The transmissions of the polarization up and down states between crossed polars are recorded as a function of the rotation angle  $\varphi_0$ , which is the orientation of the cell with respect to the (fixed) polarization plane of the incident light. Under optically uniform and saturated switching conditions, the transmissions of up and down states are described by two  $\sin^2\varphi$  functions, which exhibit a phase shift  $\delta$  to each other of twice the tilt angle  $\Theta$ .

saturated switching of an optically uniform director configuration occurs with an azimuthal angle range of  $\Delta\Phi \approx \pi$ . It can be concluded from geometrical considerations that small deviations from these conditions due to the influence of elasticity and dielectric anisotropy do not significantly effect the result.

The data were taken on heating from 25 to 60°C and for four different amplitudes (1, 2, 3, and 4 MV m<sup>-1</sup>) of a 200-Hz electric square field. Transmission was measured at an optical wavelength of 546 nm. The spontaneous polarization was determined simultaneously by the well known triangular wave method [18].

### III. GENERALIZED LANDAU MODEL FOR THE Sm-C\*–Sm-A\* PHASE TRANSITION

In the framework of a phenomenological Landau theory, the Gibbs free energy density  $g$  of a nonchiral Sm-C phase at temperature  $T$  is given by an even power series expansion of the tilt angle  $\Theta$ , which is the primary order parameter of the Sm-C–Sm-A transition:

$$g = g_0 + \frac{1}{2}a\Theta^2 + \frac{1}{4}b\Theta^4 + \frac{1}{6}c\Theta^6, \quad a = \alpha(T - T_c). \quad (1)$$

Here  $T_c$  is the Sm-C–Sm-A second order phase transition temperature;  $a$ ,  $b$ , and  $c$  are the mean-field or Landau coefficients; and  $g_0$  is the nonsingular part of  $g$ , which is set to be zero for the following considerations. The original theory refers to the free energy density  $f$ . In order to analyze measurements at constant pressure, the free energy density  $f$  is replaced by the Gibbs free energy density

$g$ . The Landau coefficient  $a$  varies linearly with temperature and changes sign at  $T = T_c$  ( $\alpha > 0$ ). As shown by Huang and Viner [19], and Birgenau *et al.* [20], an unusually large sixth order term with  $c > 0$  has to be added to the classical Landau expansion for a second order phase transition ( $b > 0$ ) to obtain agreement with the experimental results.

Chiralization of the Sm-C phase locally involves a spontaneous polarization  $P_s$  and macroscopically a spontaneous helical deformation of the director field with wave vector  $q_0$  of the chiral Sm-C\* phase, which is a helical ferroelectric phase (“helielectric”). Consequently,  $P_s$  and  $q_0$  are chiral secondary order parameters, which must be considered besides the nonchiral and primary order parameter  $\Theta$ . The corresponding mean-field expansion was suggested by Indenbom, Pikin, and Loginov [4] and is often denoted as “classical Landau model of the Sm-C\*–Sm-A\* phase transition.”

In surface stabilized geometries, the helical superstructure of the Sm-C\* phase is elastically unwound by surface interactions resulting in an improper ferroelectric Sm-C\* configuration with a macroscopic spontaneous polarization that can be reoriented in an external electric field. In this case ( $q_0 = 0$ ), the classical Landau expansion reads as

$$g = \frac{1}{2}\alpha(T - T_c)\Theta^2 + \frac{1}{4}b\Theta^4 + \frac{1}{6}c\Theta^6 + \frac{1}{2\chi_0}P^2 - CP\Theta, \quad (2)$$

with  $P = P_s$  at zero electric field. In addition to the expansion for the nonchiral case (1), chiral interactions are considered in Eq. (2) by a term  $P^2/2\chi_0$ , which is due to the effect of dipolar ordering and entropic in origin [3], and by the bilinear coupling term ( $-CP\Theta$ ) between the primary order parameter  $\Theta$  and the secondary order parameter  $P$ . The coupling constants are the piezoelectric coefficient  $C$  and the (high frequency) dielectric susceptibility  $\chi_0$ , which is not affected by (low frequency) soft- and Goldstone-mode contributions and corresponds to the polarizability of the phase in the direction of  $P$ .

Although the classical Landau model explains the basic features of the Sm-C\* phase, it shows some systematic disagreement with experimental data concerning the temperature dependence of dielectric properties, the pitch, and the reduced polarization  $P_0 = P/\Theta$ . Therefore, Žekš [15] proposed an extended mean-field model, which is usually referred to as “generalized Landau model.” A biquadratic coupling term  $\Omega\Theta^2P^2/2$  was added, which is due to a transverse quadrupole ordering. The (nonchiral) transverse quadrupole ordering amplifies the transverse dipolar ordering and the spontaneous polarization, respectively. In the generalized Landau model, the expression for the Gibbs free energy density of an unwound system ( $q_0 = 0$ ) is given by [3]

$$g = \frac{1}{2}\alpha(T - T_c)\Theta^2 + \frac{1}{4}b\Theta^4 + \frac{1}{6}c\Theta^6 + \frac{1}{2\chi_0}P^2 - CP\Theta - \frac{1}{2}\Omega P^2\Theta^2 + \frac{1}{4}\eta P^4. \quad (3)$$

The  $\eta$  term with  $\eta > 0$  has been added to stabilize the system. A discussion on the physical origin of the  $\eta$  term

was not given. Close to  $T_c$  at small tilt angle  $\Theta$  and spontaneous polarization  $P$ , the generalized model (3) is equivalent to the classical approach (2).

#### IV. RELATION BETWEEN THE GENERALIZED LANDAU- AND MICROSCOPIC MODELS

In order to achieve an experimental approach to the coefficients of the generalized Landau expansion (3), it is useful to introduce some results of the microscopic model for the spontaneous polarization, which describes the temperature dependence of the tilt-polarization coupling. As proven by numerical calculations (see next section) the  $\eta$  term in (3) is not significant for a consistent description of our experimental data and is omitted in the following considerations:

$$g = \frac{1}{2}\alpha(T - T_c)\Theta^2 + \frac{1}{4}b\Theta^4 + \frac{1}{6}c\Theta^6 + \frac{1}{2}\left[\frac{1}{\chi_0} - \Omega\Theta^2\right]P^2 - CP\Theta. \quad (4)$$

Starting with (4), a simple relation for the spontaneous polarization  $P$  is obtained by minimizing  $g$  with respect to  $P$ :

$$\frac{\partial g}{\partial P} = \left[\frac{1}{\chi_0} - \Omega\Theta^2\right]P - C\Theta = 0, \quad (5a)$$

$$P = \frac{C\Theta}{1/\chi_0 - \Omega\Theta^2}. \quad (5b)$$

For small tilt angles  $\Theta$  with  $\Omega\Theta^2 \ll 1/\chi_0$ , Eq. (5b) results in the classical approach

$$P \approx \chi_0 C\Theta = P_0\Theta, \quad (6)$$

For larger tilt angles  $\Theta$ , Eq. (5b) may result in a nonlinear dependence of  $P$  on  $\Theta$ . The polarization calculated from (5b) is higher than those from the classical approach (6) for  $\Omega > 0$  and same values of  $\Theta$ ,  $\chi_0$ , and  $C$  and qualitatively agrees with the experimental results for the tilt angle dependence of the spontaneous polarization.

Recently, Meister and Stegemeyer [21] presented an extended microscopic model of the spontaneous polarization in ferroelectric liquid crystals. They considered dipolar and quadrupolar interactions by extending the rotational potential for the molecular long axis rotation and calculated the expectation value for  $P$  by Boltzmann statistics. With some approximations, they finally obtained

$$P = \frac{A_1}{T}\Theta + \frac{A_1 A_2}{T^2}\Theta^3. \quad (7)$$

$A_1$  and  $A_2$  are coupling constants related to dipolar ( $A_1$ ) and quadrupolar ( $A_2$ ) ordering, which are considered to be essentially independent from temperature.

For reason of comparison with the phenomenological approach, Eq. (5b) is expanded into a Taylor series in  $\Theta$ :

$$P = \chi_0 C\Theta + \chi_0^2 C\Omega\Theta^3 + O(\Theta^5). \quad (8)$$

A comparison of (7) and (8) leads to a relationship be-

tween the mean-field coefficients ( $C$ ,  $\Omega$ ) and  $A_1$ ,  $A_2$

$$C = \frac{A_1}{\chi_0} \frac{1}{T}, \quad (9a)$$

$$\Omega = \frac{A_2}{\chi_0} \frac{1}{T}. \quad (9b)$$

Consequently, the introduction of the statistical approach (7) gives some information about the temperature dependence of the mean-field coefficients  $C$  and  $\Omega$ , which hyperbolically decrease with increasing temperature.

Substituting  $C$  and  $\Omega$  of (9a) and (9b) in (7), a simple approach for the tilt and temperature dependence of the spontaneous polarization is obtained:

$$P = \frac{A_1\Theta}{T - A_2\Theta^2}. \quad (10)$$

Equation (10) gives a convenient description of experimental data with only two fit parameters  $A_1$  and  $A_2$  (cf. next section).

Replacing  $P$  by (10), the Landau expansion (4) reads

$$g = \frac{1}{2}\alpha(T - T_c)\Theta^2 + \frac{1}{4}b\Theta^4 + \frac{1}{6}c\Theta^6 - \frac{A_1^2\Theta^2}{\chi_0 T(T - A_2\Theta^2)} + \frac{1}{2\chi_0} \left[1 - \frac{A_2\Theta^2}{T}\right] \frac{A_1^2\Theta^2}{(T - A_2\Theta^2)^2}. \quad (11)$$

An expansion of (11) into a power series of  $\Theta$  results in

$$g = \frac{1}{2} \left[ \alpha(T - T_c) - \frac{A_1^2}{\chi_0 T^2} \right] \Theta^2 + \frac{1}{4} \left[ b - \frac{2A_1^2 A_2}{\chi_0 T^3} \right] \Theta^4 + \frac{1}{6} \left[ c - \frac{3A_1^2 A_2^2}{\chi_0 T^4} \right] \Theta^6 + O(\Theta^8). \quad (12)$$

This equation brings up a remarkable analogy to the Landau expansion (1) for the nonchiral Sm-C phase, if *chiral Landau coefficients*  $a^*$ ,  $b^*$ , and  $c^*$  are introduced:

$$g = \frac{1}{2}a^*\Theta^2 + \frac{1}{4}b^*\Theta^4 + \frac{1}{6}c^*\Theta^6, \quad (13)$$

with

$$a^* = a - \frac{A_1^2}{\chi_0 T^2} = \alpha(T - T_c) - \frac{A_1^2}{\chi_0 T^2}, \quad (14a)$$

$$b^* = b - \frac{2A_1^2 A_2}{\chi_0 T^3}, \quad (14b)$$

$$c^* = c - \frac{3A_1^2 A_2^2}{\chi_0 T^4}. \quad (14c)$$

The following conclusions may be drawn from Eqs. (13) and (14a)–(14c), and (14c).

(i) The ansatz gives a unified description of chiral and nonchiral Sm-C phases. Chiral and nonchiral interactions are separated by their specific contributions to the Landau coefficients  $a^*$ ,  $b^*$ , and  $c^*$ . The only parameter which is chiral in character is the dipolar coupling constant  $A_1$ . The constant  $A_1$  vanishes for the nonchiral

case, resulting in the nonchiral Landau expansion (1) with  $a^*=a$ ,  $b^*=b$ , and  $c^*=c$ .

(ii) The Landau potential is an even function with respect to the chirality parameter  $A_1$  in accordance to the Neumann principle. The invariance  $g(A_1) = g(-A_1)$  means that a  $S$  enantiomer has the same effect on the potential as the corresponding  $R$  enantiomer. The mirror symmetry of the potential reflects the relationship between the  $R$  and  $S$  configuration.

(iii) The chiral Landau coefficients  $a^*$ ,  $b^*$ , and  $c^*$  are temperature dependent through their chiral contributions. The temperature dependence of the chiral contributions is related to the influence of the thermal energy  $kT$  on the bias of rotation around the molecular long axis, which leads to the spontaneous polarization of the chiral Sm- $C^*$  phase. In earlier papers [22,23] we neglected the biquadratic coupling [ $\Omega=0$  and  $A_2=0$ , cf. Eq. (9b)] and its temperature dependence. In this case, the nonchiral coefficients  $b$  and  $c$  appear to be temperature dependent.

(iv) The chiral Landau coefficients  $a^*$ ,  $b^*$ , and  $c^*$  are always smaller than the nonchiral coefficients  $a$ ,  $b$ , and  $c$  [cf. Eq. (14a)–(14c)], because  $A_1^2$  (or  $C^2$ ),  $A_2$  (or  $\Omega$ ),  $T$ , and  $\chi_0$  are always positive. Considering (14b), the (so far hypothetical) case is possible of a racemic mixture with a second order Sm- $A$ –Sm- $C$  phase transition ( $b > 0$ ), while the Sm- $A^*$ –Sm- $C^*$  transition of a corresponding enantiomer is a first order phase transition with  $b^* < 0$ .

Finally, if the Sm- $C^*$  phase is placed in an electric field of strength  $E$ , which points parallel to the direction of spontaneous polarization, the electrostatic energy  $-PE$  of the polarization-field coupling has to be added:

$$g = \frac{1}{2}a^*\Theta^2 + \frac{1}{4}b^*\Theta^4 + \frac{1}{6}c^*\Theta^6 - PE. \quad (15)$$

Restricting the discussion to the spontaneous part of the total polarization ( $P \approx P_s$ ) and applying Eqs. (7) and (14a)–(14c), the energy density of an unwound Sm- $C^*$  sample in an electric field  $E$  reads fully expanded

$$\begin{aligned} g = & - \left[ \frac{A_1 E}{T} \right] \Theta + \frac{1}{2} \left[ \alpha(T - T_c) - \frac{A_1^2}{\chi_0 T^2} \right] \Theta^2 \\ & - \left[ \frac{A_1 A_2 E}{T^2} \right] \Theta^3 + \frac{1}{4} \left[ b - \frac{2A_1^2 A_2}{\chi_0 T^3} \right] \Theta^4 \\ & + \frac{1}{6} \left[ c - \frac{3A_1^2 A_2^2}{\chi_0 T^4} \right] \Theta^6. \end{aligned} \quad (16)$$

If the tilt angle  $\Theta$  is determined for various temperatures  $T$  and electric field strengths  $E$ , any measured ( $T$ ,  $E$ ,  $\Theta$ ) triplet has to minimize the energy density (16) and has to be a real root of the energy densities first derivative with respect to  $\Theta$ :

$$\begin{aligned} - \left[ \frac{A_1 E}{T} \right] + \left[ \alpha(T - T_c) - \frac{A_1^2}{\chi_0 T^2} \right] \Theta - 3 \left[ \frac{A_1 A_2 E}{T^2} \right] \Theta^2 \\ + \left[ b - \frac{2A_1^2 A_2}{\chi_0 T^3} \right] \Theta^3 + \left[ c - \frac{3A_1^2 A_2^2}{\chi_0 T^4} \right] \Theta^5 = 0 \end{aligned} \quad (17)$$

It is possible to obtain the nonchiral Landau coefficients

numerically by searching for  $\alpha$ ,  $b$ , and  $c$  values for which all ( $T$ ,  $E$ ,  $\Theta$ ) triplets determined in experiments minimize the energy density (16). In principle  $A_1$  and  $A_2$  could be fitted also by this procedure. But in order to reduce the total number of fit parameters and to increase the significance of such an evaluation, it is more convenient to determine  $A_1$  and  $A_2$  by an independent experiment.

## V. SPONTANEOUS POLARIZATION DATA

To obtain the coupling coefficients  $A_1$  and  $A_2$ , which are related to the bilinear and biquadratic coupling coefficients  $C$  and  $\Omega$  [cf. (9a) and (9b)], the temperature and tilt angle dependence of the spontaneous polarization was investigated and analyzed according to Eq. (10). The absolute value of the spontaneous polarization was determined by the triangular field reversal method [18] at several temperatures and the corresponding tilt angle by the method from Bahr and Heppke [17]. Both methods require the application of an electric field. It is important to note, that (7) and (10) are derived for zero electric field. The spontaneous polarization does not depend on the electric field strength by definition, but, due to the electroclinic effect, the tilt angle does. Therefore, the tilt angle was measured at several field strengths (1, 2, 3, and 4 MV m<sup>-1</sup>) and carefully extrapolated to  $E=0$  MV m<sup>-1</sup>.

The spontaneous polarization  $P_s$  is plotted in Fig. 3(a) vs the tilt angle  $\Theta$  (extrapolated to  $E=0$  MV m<sup>-1</sup>) and in Fig. 3(b) vs the temperature  $T$ . The essentially nonlinear dependence of  $P_s(\Theta)$  in Fig. 3(a) visualizes that the linear approach (6), which results from the classical Landau model, is insufficient for a realistic description of the experimental data.

The solid lines in Figs. 3(a) and 3(b) represent the best fit to the experimental data according to the advanced approach (10). The best fit was obtained with  $A_1=0.322$  CK m<sup>-2</sup> and  $A_2=542$  K. Especially Fig. 3(b) demonstrates that Eq. (10) gives an excellent description of the experimental  $P_s$  data over a wide temperature range of about 40 K. It should be emphasized that the fit of  $P_s(T)$  in Fig. 3(b), which needs only two fit parameters ( $A_1, A_2$ ), exhibits at least the same quality as a power law fit  $P_s = P_0(T_c - T)^\beta$ , which involves three fit parameters ( $P_0, T_c, \beta$ ).

The experimental data in Fig. 3 demonstrate that the spontaneous polarization does not saturate even at temperatures far below the Sm- $A^*$ –Sm- $C^*$  phase transition. This behavior explains that the data can be consistently described without the  $\eta P^4$  term of the generalized Landau expansion (3). As recently shown by Gouda *et al.* [24], this term is related to a low temperature saturation of  $P_s$  and therefore is not relevant for our system.

## VI. TILT ANGLE DATA

The director tilt angles of FLC 6430 at four different electric field strengths ( $E=1, 2, 3$ , and 4 MV m<sup>-1</sup>) and in the vicinity of the Sm- $C^*$ –Sm- $A^*$  phase transition between 328.15 and 333.15 K are depicted in Fig. 4. An overall large electroclinic effect is observed, which is almost linear to the electric field strength at temperatures

above 332 and below 329 K. But close to the phase transition where the harmonic Landau term  $\alpha(T - T_c)\Theta^2/2$  vanishes, the electroclinic response is nonlinear as a function of the electric field strength and predominantly governed by the coefficients  $b$  and  $c$  of the higher order expansion terms.

The solid lines in Fig. 4 result from the best fit of the Landau expansion (16) to the experimental data. In the vicinity of the phase transition, the Landau expansion (16) gives an excellent description of the director tilt angle with only three fit parameters ( $\alpha$ ,  $b$ ,  $c$ ) and as a function of the temperature as well as the electric field strength with  $\alpha = 26.5 \text{ kJ m}^{-3} \text{ K}^{-1}$ ,  $b = 66.9 \text{ kJ m}^{-3}$ , and  $c = 8010 \text{ kJ m}^{-3}$ . The parameters  $A_1$  and  $A_2$  were set to the values described in the previous paragraph and  $T_c$  and  $\chi_0$  were taken from experimental measurements ( $T_c = 330.15 \text{ K}$ ,  $\chi_{0,r} = 8.4$ ; the value of  $\chi_{0,r}$  was determined by J. Schacht and W. Kuczynski at the Institute of Molecular Physics, Poznan, Poland). As  $T_c$  is concerned, it was allowed to be refined in a small range of  $330.15 \pm 0.50 \text{ K}$ , because the experimentally observed  $\text{Sm-C}^* - \text{Sm-A}^*$  transition temperature does not exactly

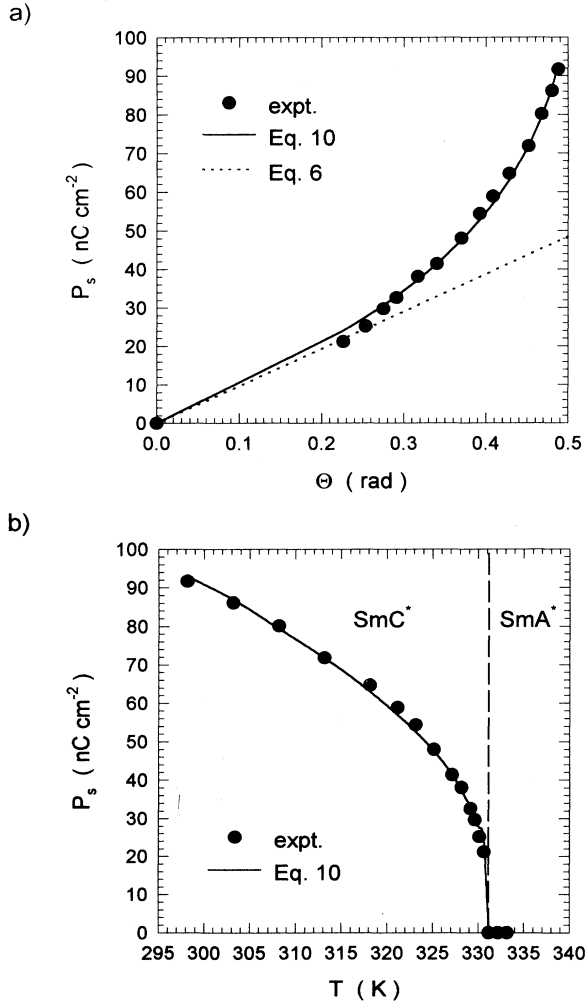


FIG. 3. Spontaneous polarization  $P_s$  of FLC 6430 as a function of the tilt angle  $\Theta$  (a) and of the temperature  $T$  (b).

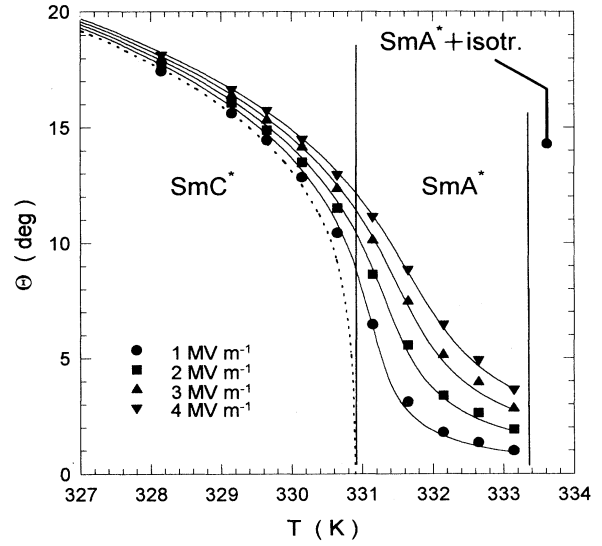


FIG. 4. Director tilt angles  $\Theta$  of FLC 6430 in the vicinity of the  $\text{Sm-C}^* - \text{Sm-A}^*$  phase transition as a function of the temperature  $T$  and at various electric field strengths. The solid lines represent the best fit according to the generalized mean-field model [Eq. (16)]. The dotted line represents the tilt angle at zero electric field conditions.

match  $T_c$ , which is the transition temperature of the corresponding nonchiral  $\text{Sm-C} - \text{Sm-A}$  transition. The best fit was obtained for  $T_c = 330.45 \text{ K}$ .

All parameters of the Landau expansion (16) for FLC 6430 are collected in Table I and compared to the results of other investigations on different compounds [8–10, 14]. Generally, the values for FLC 6430, which to our knowledge is the first FLC mixture investigated with respect to its Landau coefficients, are in the same range as other values listed in Table I. The relatively small  $\alpha$  value results from the large electroclinic effect of FLC 6430, which is discussed in more detail in the next section. The coefficient  $b$  of the fourth order expansion term is only 30% of the one Huang and co-workers [9,10] determined for DOBAMBC. This small  $b$  value supports that the  $\text{Sm-C}^* - \text{Sm-A}^*$  transition of FLC 6430 comes close to a first order phase transition with  $b < 0$  as found by Bahr, Heppke, and Sabaschus [14] for the compound  $L-7$ . An unusually large sixth order expansion term and a high  $c$  coefficient is necessary for a description of the experimental data. This fact involves some serious problems concerning the convergence of the Landau expansion. The large value of the biquadratic coupling coefficient  $\Omega$  found by Huang and co-workers [9,10] for DOBAMBC might be due to the existence of a higher ordered ferroelectric phase below the  $\text{Sm-C}^*$  phase in this case. These findings are confirmed for FLC compounds with higher ordered phases where we also find larger values of  $\Omega$  and  $A_2$ .

## VII. ELECTROCLINIC EFFECT

The electroclinic effect of a chiral smectic phase is related to the director soft mode and describes the tilt angle

variation  $\delta\Theta$ , which is induced by an electric field in a direction perpendicular to the electric field vector (cf. Fig. 1):

$$\delta\Theta(T, E) = \Theta(T, E) - \Theta(T, E=0). \quad (18)$$

The electroclinic effect depends on temperature  $T$  and field strength  $E$ . An evaluation of the electroclinic effect has to rely on the field-dependent tilt angle data  $\Theta(T, E)$  discussed in Sec. VI and the tilt angle at zero electric field strength  $\Theta(T, E=0)$ .

In order to estimate the tilt angles  $\Theta(T, E=0)$  from the field-dependent data  $\Theta(T, E)$  without application of a more or less arbitrary extrapolation procedure, Eq. (17) was solved numerically for  $E=0$  with the values of the Landau coefficients  $\alpha$ ,  $b$ ,  $c$ ,  $A_1$ , and  $A_2$  discussed in the previous sections. These tilt angles are plotted as function of the temperature in Fig. 4 (dashed line). At  $T \geq 330.9$  K the tilt vanishes, which indicates the Sm- $C^*$ -Sm- $A^*$  phase transition.

The electroclinic effect was then calculated according to Eq. (18) and plotted as a function of temperature in Fig. 5 for four different strengths of the electric field. The electroclinic effect exhibits a pronounced maximum at the Sm- $C^*$ -Sm- $A^*$  phase transition and clearly shows a nonlinear behavior with respect to the electric field strength between 330 and 332 K (Fig. 5).

The electroclinic effect is closely related to the soft-mode susceptibility  $\chi_{sm}$ , which is observed in dielectric dispersion experiments [24–26]. Therefore, the overall shape of the curves in Fig. 5 strongly resembles the temperature dependence of the soft-mode dielectric contribution. Generally, it is very difficult to obtain values of the soft-mode contribution of the Sm- $C^*$  phase by dielectric measurements because this soft mode is strongly superim-

posed by the ferroelectric Goldstone-mode contribution, which has to be suppressed by a large bias field [25]. In contrast to dielectric methods, the optical measurement of the electroclinic effect used in this paper easily allows us to measure the Sm- $C^*$  soft-mode behavior and should be considered as a useful complement of dielectric investigations.

In analogy to the analysis of dielectric data [25], the reciprocal electroclinic effect  $(\delta\Theta)^{-1}$ , which is related to the reciprocal soft-mode susceptibility  $(\chi_{sm})^{-1}$ , is plotted as function of the reduced temperature  $T - T_c$  in Fig. 6. For temperatures  $T - T_c > 0$  K (Sm- $A^*$  phase) the reciprocal electroclinic effect decreases linearly with the temperature towards  $T_c$ . But in the Sm- $C^*$  phase at  $T - T_c < 0$  K, a strong nonlinear increase is observed (cf. Fig. 6). As recently shown by Gouda *et al.* [24], this nonlinearity reflects the evidence of the biquadratic coupling term. A further analysis in terms of the generalized Landau model on the correlation between the electroclinic effect obtained by optical measurements and the soft-mode susceptibility obtained from dielectric dispersion measurements is in progress.

## VIII. THERMODYNAMIC FUNCTIONS

Assuming a density of  $1 \text{ g cm}^{-3}$ , the specific Gibbs free energy  $g(T) - g_0$  in the vicinity of the Sm- $C^*$ -Sm- $A^*$  phase transition was calculated by minimizing Eq. (16) for a given temperature  $T$  at zero electric field conditions  $E=0$  and with the values of the Landau-expansion coefficients for FLC 6430 as described in the previous sections. The results are shown by the solid line in Fig. 7. The specific Gibbs free energy passes the phase transition temperature continuously. Also its first negative temper-

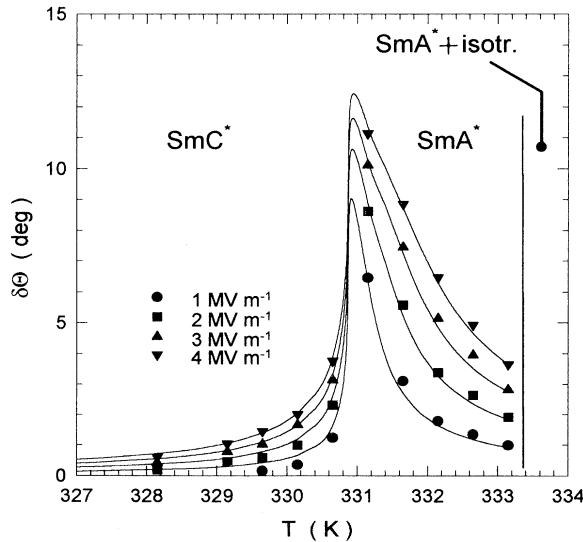


FIG. 5. Electroclinic effect  $\delta\Theta$  of FLC 6430 in the vicinity of the Sm- $C^*$ -Sm- $A^*$  phase transition as a function of temperature  $T$  and at various electric field strengths. The solid lines represent the best fit according to the generalized mean-field model [Eq. (16)].

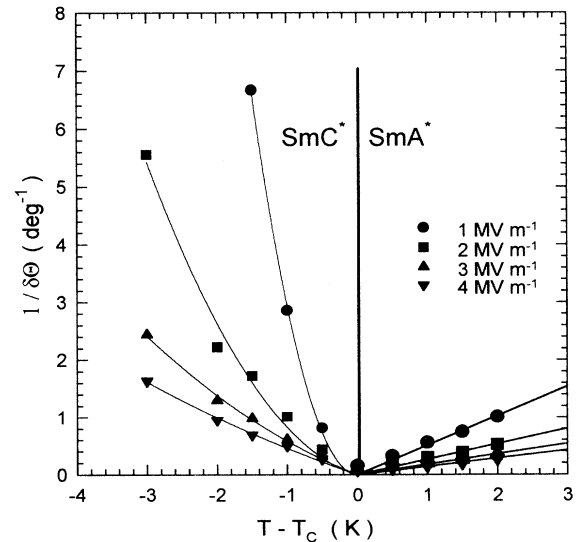


FIG. 6. Reciprocal electroclinic effect  $1/\delta\Theta$  of FLC 6430 in the vicinity of the Sm- $C^*$ -Sm- $A^*$  phase transition as a function of temperature  $T$  and at various electric field strengths. The solid lines represent the best fit according to the generalized mean-field model [Eq. (16)].  $1/\delta\Theta$  is related to the reciprocal soft-mode dielectric susceptibility  $1/\chi_{sm}$ .

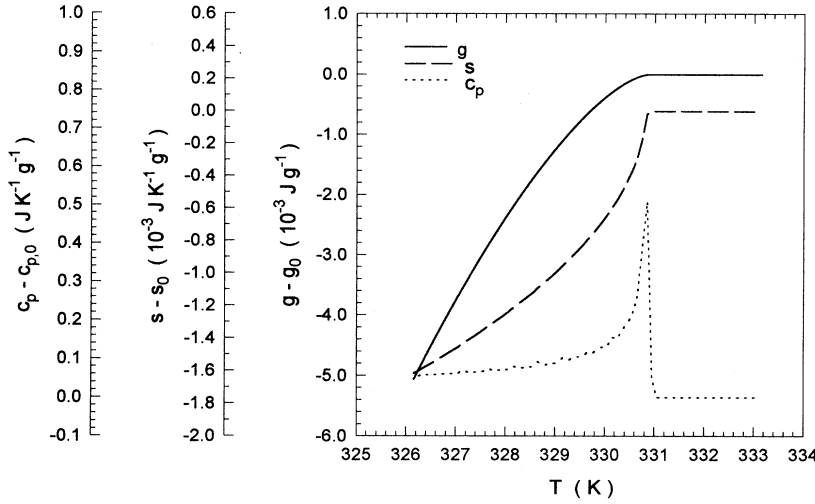


FIG. 7. Thermodynamic functions of FLC 6430 in the vicinity of the Sm-C\*-Sm-A\* phase transition. The nonsingular part of the specific Gibbs free energy  $g$ , the specific entropy  $s$ , and the specific heat capacity  $c_p$  are plotted as a function of temperature  $T$ . The functions are obtained from the generalized mean-field model [Eq. (16)] with coefficients listed in Table I (density  $\rho = 1 \text{ g cm}^{-3}$ ).

ature derivative, which is the entropy density  $s$ ,

$$s = - \left[ \frac{\partial g}{\partial T} \right]_p \quad (19)$$

passes  $T_c$  in a continuous way (dashed line in Fig. 7). But the second temperature derivative of  $g$  or the first temperature derivative of  $s$ , which is related to the specific heat capacity at constant pressure  $c_p$  by

$$c_p = T \left[ \frac{\partial s}{\partial T} \right]_p = -T \left[ \frac{\partial^2 g}{\partial T^2} \right]_p, \quad (20)$$

exhibits a (logarithmic) singularity at the phase transition temperature (dotted line in Fig. 7). According to the Ehrenfest classification, the Sm-C\*-Sm-A\* phase transition of FLC 6430 has to be considered as a second order phase transition.

The heat capacity data depicted in Fig. 7 and obtained from a fit of the Landau model (17) to electro-optical tilt angle data are compared to differential scanning calorimetric (DSC) measurements in Fig. 8. At a very small scanning rate of  $1 \text{ K min}^{-1}$ , the DSC method is not able to resolve the singularity of  $c_p$ , which is smeared out. Only a small “peak” is observed. If the  $c_p$  singularity actually exists, their shape should be investigated by high-resolution ac calorimetry. The  $c_p$  jump related to the Sm-C\*-Sm-A\* phase transition with  $\Delta c_p < 0$ , which is observed in the DSC experiment, correlates nicely with the Landau model (17). Therefore, the calorimetric measurements provide an independent check of the consistency of the Landau model (17) and its fit to electro-optical tilt angle data.

## IX. CHIRALITY

In terms of the generalized Landau approach, the chirality of a helically unwound Sm-C\* and a Sm-A\* phase is related to the bilinear coupling coefficients  $C$  [Eq. (4)] and  $A_1$  [Eq. (12)], respectively, which vanishes for nonchiral systems and describes a spontaneous dipolar ordering for chiral systems. Quadrupolar ordering spontaneously occurs in chiral and nonchiral systems as

well. Therefore, the biquadratic coupling coefficients  $\Omega$  [Eq. (4)] and  $A_2$  [Eq. (12)], respectively, are nonchiral in character.

The formulation of the generalized Landau approach (12) allows a simple separation of chiral ( $g^*$ ) and nonchiral ( $g^\circ$ ) contributions to the total Gibbs energy density:

$$g(T) = g^\circ(T) + g^*(T), \quad (21)$$

with

$$g^\circ(T) = \frac{1}{2}\alpha(T - T_c)\Theta^2 + \frac{1}{4}b\Theta^4 + \frac{1}{6}c\Theta^6, \quad (22)$$

and

$$g^*(T) = -\frac{A_1^2}{2} \left[ \frac{1}{\chi_0 T^2} \Theta^2 + \frac{A_2}{\chi_0 T^3} \Theta^4 + \frac{A_2^2}{\chi_0 T^4} \Theta^6 \right]. \quad (23)$$

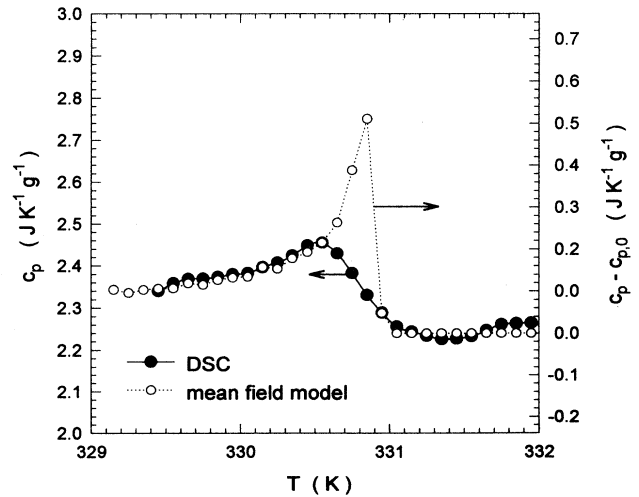


FIG. 8. Comparison between specific heat capacity data of FLC 6430 from the generalized mean-field model [Eq. (16)] and differential scanning calorimetry (DSC).  $c_p$ , specific heat capacity;  $T$ , temperature.



The functions  $g(T)$ ,  $g^{\circ}(T)$ , and  $g^*(T)$  apply for zero electric field conditions according to Eqs. (21)–(23). The tilt angles at zero electric field are depicted in Fig. 4 and the coefficients  $\alpha$ ,  $T_c$ ,  $b$ ,  $c$ ,  $A_1$ , and  $A_2$  for FLC 6430 are given in Table I. The functions are plotted in Fig. 9, which shows a cusplike maximum of the nonchiral interaction energy  $g^{\circ}$  just below the chiral  $\text{Sm-C}^*-\text{Sm-A}^*$  phase transition. Consequently, in this temperature range the  $\text{Sm-C}^*-\text{Sm-A}^*$  phase transition, which is represented by a decrease of the total energy density  $g$ , is driven by chiral interactions whose energy density  $g^*$  exhibits a steep decrease just below this transition temperature.

The tilt angles and the Gibbs free energy density of a nonchiral system that corresponds to FLC 6430 can be estimated by minimizing Eq. (21) with  $A_1=0$  or  $g^*=0$ . (A nonchiral system that corresponds to FLC 6430 should be obtained, if all chiral components of the FLC 6430 mixture are added in racemic composition.) The results of this estimation are plotted in Fig. 10 and compared to the results for the chiral FLC 6430 mixture. Figure 10 shows that the phase transition of the nonchiral system shifts about  $-0.4$  K in temperature with respect to the phase transition of the chiral system. This result agrees with investigations on chiral-racemic phase diagrams for other systems [14,27]. But not only the phase transition temperature is shifted by chirality, also the slope of the  $\Theta(T)$  curve is slightly modified. Meyer [28] showed in an early analysis on the influence of chirality on the  $\text{Sm-C}^*-\text{Sm-A}^*$  phase transition, which was based on the classical Landau approach, that chirality only affects the  $a\Theta^2/2$  term and results only in a temperature shift of the phase transition. In our formulation, which is now based on the generalized Landau approach, chirality affects all terms of the nonchiral Landau expansion [cf. Eqs. (1) and (14a)–(14c)] and therefore

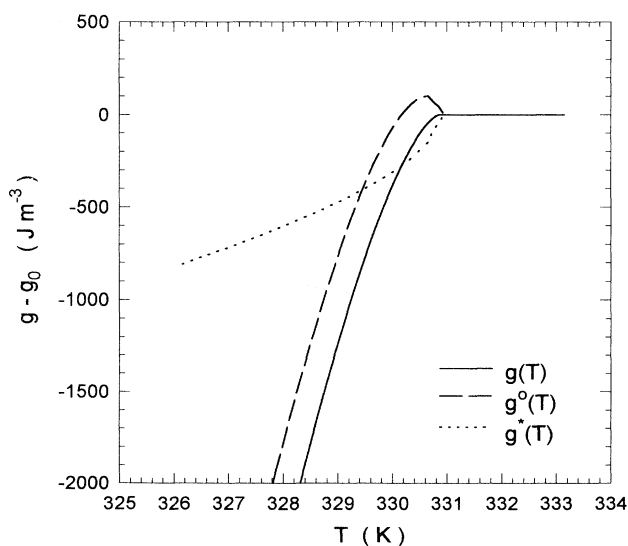


FIG. 9. Chiral ( $g^*$ ) and nonchiral ( $g^{\circ}$ ) contributions to the total Gibbs free energy density ( $g$ ) of FLC 6430 as a function of temperature  $T$ .

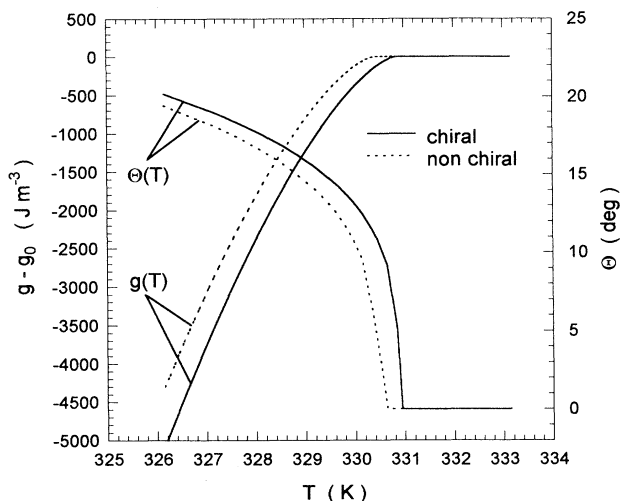


FIG. 10. Effect of chirality on the Gibbs free energy density  $g$  and the tilt angle  $\Theta$  as a function of temperature  $T$ .

should also affect the shape of the  $\Theta(T)$  curve as shown in Fig. 10. Unfortunately, this consideration could not be checked experimentally, because a nonchiral mixture that corresponds to FLC 6430 is not available.

#### X. EXTENSION TO TEMPERATURES FAR BELOW $T_c$

According to the spirit of the Landau theory, the generalized mean-field approach of the  $\text{Sm-C}^*-\text{Sm-A}^*$  transition expands the energy density into a power series of the order parameter with expansion coefficients  $\alpha$ ,  $b$ , and  $c$  that are *independent* from temperature. But if the same approach is applied for a description of the order parameter and the energy density at temperatures far away from the phase transition, the Landau coefficients must be considered as parameters *smoothly* varying with temperature [29].

Electric field-dependent tilt angle measurements on a wide temperature range of about 35 K between room temperature and clearing temperature of FLC 6430 are depicted in Fig. 11. According to the considerations above, it is not surprising that the Landau model (16) with temperature-independent coefficients listed in Table I fails for temperatures far below the phase transition (cf. dotted lines in Fig. 11). In order to improve the description for these temperatures, a linear temperature dependence of the nonchiral coefficients  $b$  and  $c$  was introduced by

$$b(T) = \beta_0 + \beta(T - T_c), \quad (24)$$

$$c(T) = \gamma_0 + \gamma(T - T_c). \quad (25)$$

Application of this slightly modified approach leads to an excellent description of the field-dependent tilt angle behavior over the complete temperature range (solid lines in Fig. 11). Differences between experimental data and fit are well below  $1^\circ$ . In order to achieve this slight modification, which is consistent with the treatment in Sec. V and VI, the values of  $A_1$ ,  $A_2$ ,  $\chi_0$ , and  $T_c$  were set

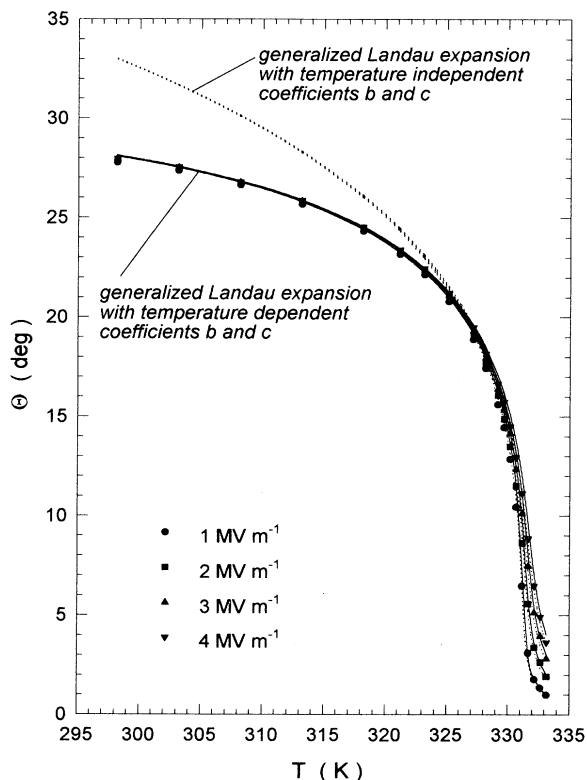


FIG. 11. Extension of the generalized Landau expansion to temperatures far below  $T_c$ . The Landau expansion for the Sm-C\*-Sm-A\* phase transition describes the director tilt angle  $\Theta$  at temperatures  $T$  far below the phase transition temperature  $T_c$ , if a smooth temperature dependence of the Landau coefficients  $b$  and  $c$  is introduced.

to the values given in Table I. Values of  $\alpha$ ,  $\beta_0$ , and  $\gamma_0$  were restricted to a  $\pm 20\%$  range of the corresponding values, which were found for  $\alpha$ ,  $b$ , and  $c$  at  $T \approx T_c$  in the vicinity of the phase transition as described in Sec. VI and listed in Table I. With these constraints, the best fit shown in Fig. 11 was achieved with the following values:

$$\alpha = 24.4 \text{ kJ m}^{-3} \text{ K}^{-1},$$

$$\beta_0 = 52.4 \text{ kJ m}^{-3}, \quad \beta = -5.03 \text{ kJ m}^{-3} \text{ K}^{-1},$$

$$\gamma_0 = 6712 \text{ kJ m}^{-3}, \quad \gamma = -207 \text{ kJ m}^{-3} \text{ K}^{-1}.$$

The Landau coefficient  $a = \alpha(T - T_c)$  increases with increasing temperature, while the higher order coefficients  $b$  and  $c$  are found to be slightly decreasing with increasing temperature, as concluded from  $\alpha$ ,  $\beta$ , and  $\gamma$ . The

temperature variation per Kelvin of the coefficients  $b$  and  $c$  makes less than 10% of their values at the phase transition.

## XI. CONCLUSIONS

Electro-optical data on the temperature dependence of the tilt angle and the electroclinic effect of the Sm-C\* and the Sm-A\* phase of FLC 6430 can consistently be described by the generalized Landau expansion for a helically unwound sample, which was reformulated to some extent in terms of the statistical approach of Meister and Stegemeyer [21]. The consistency and agreement found supports the evidence of quadrupolar ordering for the understanding of the Sm-C\*-Sm-A\* phase transition and the temperature dependence of the spontaneous polarization. It should be stressed that more simple approaches to describe the electroclinic effect of FLC 6430, which ignored the biquadratic coupling and the quadrupolar interaction failed. The fit of the Landau model to the experimental data provides values of all mean-field coefficients involved in a description of a helically unwound Sm-C\* phase. The values obtained agree with values from high-resolution ac calorimetry.

The evaluation carried out in this paper requires only a standard experimental setup for electro-optical investigations and measurements of the spontaneous polarization of FLC's. Therefore, a fast and powerful method is provided that can now be applied to study the dependence of the fundamental mean-field coefficients  $\alpha$ ,  $b$ ,  $c$ ,  $C(A_1)$ , and  $\Omega(A_2)$  with respect to the chemical constitution (e.g., in homologous series) or the composition of a FLC mixture. These data should be of particular interest for the design and the structure-property relationship of FLC compounds and for the modeling of commercial FLC mixtures.

Another point of interest concerns the separation of chiral and nonchiral interactions in FLCs. The approach outlined in Sec. IX should be experimentally verified by investigating the mean-field coefficients of chiral-racemic mixtures and an analysis of the corresponding phase diagram. The chiral and nonchiral interaction potentials may improve our knowledge of molecular interactions in liquid crystals and serve as a starting point for molecular dynamics simulations.

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- [1] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. (Paris) Lett.* **36**, 69 (1975).  
 [2] N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).  
 [3] J. W. Goodby, R. Blinc, N. A. Clark, S. T. Lagerwall, M. A. Osipov, S. A. Pikin, T. Sakurai, K. Yoshino, and B. Žekš, *Ferroelectric Liquid Crystals: Principles, Properties*

*and Applications, Ferroelectricity and Related Phenomena* Vol. 7 (Gordon and Breach, Philadelphia, 1991).

- [4] V. L. Indenbom, S. A. Pikin, and E. B. Loginov, *Kristallografiya* **21**, 1093 (1976) [*Sov. Phys. Crystallogr.* **21**, 632 (1976)].  
 [5] B. Žekš, *Mol. Cryst. Liq. Cryst.* **114**, 259 (1984).  
 [6] M. A. Osipov and S. A. Pikin, *Mol. Cryst. Liq. Cryst.* **103**,

- 57 (1983).
- [7] B. Urbanc and B. B. Žekš, *Liq. Cryst.* **5**, 1075 (1989).
- [8] T. Carlsson and I. Dahl, *Mol. Cryst. Liq. Cryst.* **95**, 373 (1983).
- [9] S. Dumrongrattana, C. C. Huang, G. Nounesis, S. C. Lieu, and J. M. Viner, *Phys. Rev. A* **34**, 5010 (1986).
- [10] C. C. Huang and S. Dumrongrattana, *Phys. Rev. A* **34**, 5020 (1986).
- [11] T. Chan, Ch. Bahr, G. Heppke, and C. W. Garland, *Liq. Cryst.* **13**, 667 (1993).
- [12] S. Garoff and R. B. Meyer, *Phys. Rev. Lett.* **38**, 848 (1977).
- [13] G. Andersson, I. Dahl, W. Kuczynski, S. T. Lagerwall, K. Skarp, and B. Stebler, *Ferroelectrics* **84**, 285 (1988).
- [14] Ch. Bahr, G. Heppke, and B. Sabaschus, *Ferroelectrics* **84**, 103 (1988).
- [15] J. Fünfschilling and M. Schadt, *Jpn. J. Appl. Phys.* **30**, 741 (1991).
- [16] K. H. Yang, T. C. Chieu, and S. Osofsky, *Appl. Phys. Lett.* **55**, 125 (1989).
- [17] Ch. Bahr and G. Heppke, *Liq. Cryst.* **2**, 825 (1987).
- [18] K. Miyasato, S. Abe, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys. Lett.* **22**, L-661 (1983).
- [19] C. C. Huang and J. M. Viner, *Phys. Rev. A* **25**, 3385 (1982).
- [20] R. J. Birgenau, C. W. Garland, A. R. Kortan, J. D. Lister, M. Meichle, B. M. Ocko, C. Rosenblatt, L. J. Yu, and J. W. Goodby, *Phys. Rev. A* **27**, 1251 (1983).
- [21] R. Meister and H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.* **97**, 1242 (1993).
- [22] F. Gießelmann and P. Zugenmaier, *Liq. Cryst.* **14**, 389 (1993).
- [23] F. Gießelmann and P. Zugenmaier, *Mol. Cryst. Liq. Cryst.* **237**, 121 (1993).
- [24] F. Gouda, T. Carlsson, G. Andersson, S. T. Lagerwall, and B. Stebler, *Liq. Cryst.* **16**, 315 (1994).
- [25] F. Gouda, K. Skarp, and S. T. Lagerwall, *Ferroelectrics* **113**, 165 (1991).
- [26] F. Gouda, K. Skarp, and S. T. Lagerwall, *Mol. Cryst. Liq. Cryst.* **209**, 99 (1991).
- [27] J. Schacht, Diploma thesis, TU Clausthal, 1993.
- [28] R. B. Meyer, *Mol. Cryst. Liq. Cryst.* **90**, 33 (1977).
- [29] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, Oxford, 1971).