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Behavior of ferroelectric liquid crystals in external fields

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It is shown that the reentrant Sm-C^* phase in an external magnetic as well as in an external electric field in typical ferroelectric liquid-crystalline compounds, such as p-(n-decyloxybenzylidene)-p'-amino-(2-methylbutyl) cinnamate (DOBAMBC), has the same physical origin as the anomalous temperature dependence of the pitch p. The observed temperature dependence of the critical electric field E_c is described well within the extended Landau model using *the same values of the model parameters* as in the magnetic-field case [Phys. Rev. E **48**, 455 (1993)]. In DOBAMBC a simple relationship between E_c, the tilt Θ, the polarization P, and the pitch p in a zero field $E_c \propto \Theta^2/(P p^2)$ is found to be valid at all temperatures except for $T_c - T \lesssim 0.1$ K. At temperatures 0.2 mK$< T_c - T <$ 2.5 mK, where the Sm-C^* $\leftrightarrow$Sm-C transition is first order, the stability limits of both phases are determined: the associated hysteresis is found to be small.

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An external electric or magnetic field applied perpendicular to the helical axis in the ferroelectric smectic-C^* (Sm-C^*) phase unwinds the helix and thus induces the phase transition from the modulated Sm-C^* to the homogeneously tilted and polarized smectic-C (Sm-C) phase, if the field strength exceeds the critical value. Since the prediction and discovery of ferroelectricity in the Sm-C^* phase by Meyer *et al.* in 1975 [1], the influence of external fields has been investigated experimentally and theoretically, but the behavior of ferroelectric liquid crystals in external fields has not been theoretically understood completely [2]. Basically, there have been questions related to the origin of the nonmonotonic temperature dependence of the critical magnetic and the critical electric field (leading in both cases to the reentrance of the Sm-C^* phase: on decreasing the temperature the phase sequence Sm-$C^*\rightarrow$Sm-C $\rightarrow$Sm-C^* appears).

The compound in which ferroelectric liquid-crystalline behavior was found first [1] is p-(n-decyloxy benzylidene)-p'-amino-(2-methylbutyl) cinnamate (DOBAMBC). On lowering the temperature from the high-temperature smectic-A (Sm-A) phase, where the molecular director is perpendicular to smectic layers, the phase transition into the ferroelectric Sm-C^* phase occurs at the critical temperature $T_c \approx 95°$C. In this paper we give some comments and present some results to elucidate the theoretical understanding of the problem described above, i.e., the reentrant Sm-C^* phase in external fields in the compound DOBAMBC, which exhibits typical ferroelectric liquid-crystalline behavior.

A critical field is the field that unwinds the helical structure. One would expect the critical field to be related to the pitch length: the larger the pitch, the lower the critical field. Such a relationship has been actually observed by Muševič *et al.* [3], who measured the critical magnetic field H_c in dependence on the temperature and made a comparison to the temperature dependence of the pitch p. A simple relationship $H_c \propto 1/p$ has been found to be valid at all temperatures, where H_c has been determined for pure chiral DOBAMBC as well as for a mixture of chiral and racemic DOBAMBC. In the latter the pitch p is increased with respect to the pure sample and the critical field H_c is correspondingly smaller.

As for the temperature dependence of the pitch in chiral DOBAMBC [4–8], all measurements yield the following behavior: on lowering the temperature from T_c, the pitch increases sharply, reaches a maximum at about $T_c - T \sim 1$ K, and decreases on lowering the temperature farther. As such an anomalous behavior of the pitch was not expected, the authors of early measurements [4] were cautious about the observed sharp increase of the pitch close to T_c. All later experiments [5–7], including the high-temperature resolution measurements [8], clearly confirmed the above behavior. Although the helical pitch is found to depend on the thickness [5,7] and on the sample geometry [4] (bookshelf or homeotropic), its temperature dependence is qualitatively the same in all cases.

Also the critical-electric-field measurements on DOBAMBC [9,6,7,10,11] yield a nonmonotonic temperature dependence of the critical electric field. On lowering the temperature from above T_c this leads to the phase sequence Sm-C $\rightarrow$Sm-$C^*\rightarrow$Sm-C $\rightarrow$Sm-C^*. Although the minimum of the critical electric field E_c takes place about 1 K below T_c, i.e., approximately where the pitch p assumes the maximum, from the experimental point of view the relationship between E_c and p is not as obvious as in the case of the critical magnetic field H_c.

We will introduce briefly the Landau model [12] in its extended form [13–16]. In a Landau description of the Sm-$A\leftrightarrow$Sm-C^* phase transition two order parameters are used: a tilt $\vec{\xi}=(\xi_1,\xi_2)$, which is a projection of the director into the smectic plane, and the in-plane polarization $\vec{P}=(P_x,P_y)$. In the absence of external fields the free energy density $f(z)$ (the z axis is chosen along the helical axis) can be expanded with respect to both order parameters

$$f(z)=\frac{a}{2}\left(\xi_1^2+\xi_2^2\right)+\frac{b}{4}\left(\xi_1^2+\xi_2^2\right)^2+\frac{c}{6}\left(\xi_1^2+\xi_2^2\right)^3-\Lambda\left(\xi_1\frac{d\xi_2}{dz}-\xi_2\frac{d\xi_1}{dz}\right)-d(\xi_1^2+\xi_2^2)\left(\xi_1\frac{d\xi_2}{dz}-\xi_2\frac{d\xi_1}{dz}\right)$$
$$+\frac{K_3}{2}\left[\left(\frac{d\xi_1}{dz}\right)^2+\left(\frac{d\xi_2}{dz}\right)^2\right]+\frac{1}{2\epsilon}\left(P_x^2+P_y^2\right)+\frac{\eta}{4}(P_x^2+P_y^2)^2-\mu\left(P_x\frac{d\xi_1}{dz}+P_y\frac{d\xi_2}{dz}\right)-C\left(P_x\xi_2-P_y\xi_1\right)$$
$$-\frac{\Omega}{2}(P_x\xi_2-P_y\xi_1)^2\,, \tag{1}$$

where only the first coefficient a is temperature dependent. In an external magnetic field $\vec{H}$ the quadratic coupling is $-\epsilon_a(\vec{H}\cdot\vec{\xi})^2/2$ (ϵ_a is a diamagnetic anisotropy), whereas in an external electric field $\vec{E}$ the linear coupling is $-\vec{E}\cdot\vec{P}$ has to be added to the expansion (1). The above model reduces to a simple Pikin-Indenbom form [12] for $c=0$, $d=0$, $\eta=0$, and $\Omega=0$. The major deficiency of the Pikin-Indenbom model is that it does not account for the anomalous temperature dependence of the pitch p [8] and the ratio polarization versus tilt P/Θ [17] (here $P=|\vec{P}|$ and $\Theta=|\vec{\xi}|$ in the absence of external fields). In contrast to the Pikin-Indenbom model, where both quantities are temperature independent, the above model (1) describes the anomalous temperature dependence of p and P/Θ in agreement with experimental results [15]. The essential novelty of the above model compared to the Pikin-Indenbom model is the presence of an achiral biquadratic coupling between the tilt $\vec{\xi}$ and the polarization $\vec{P}$ [13] (the Ω term), which originates microscopically in bipolar ordering of transverse molecular axes [18]. The temperature dependence of the ratio P/Θ is as follows: just below T_c where the bilinear coupling (the C term) is dominant, $P/\Theta\sim\epsilon C$, while at lower temperatures the biquadratic coupling (the Ω term) prevails, $P/\Theta\sim\sqrt{\Omega/\eta}$. In the regime where both couplings are important the ratio P/Θ increases sharply from the value ϵC to the value $\sqrt{\Omega/\eta}$. In DOBAMBC such an increase is observed [17] about 1 K below T_c. The temperature where this sharp increase takes place is thus a result of the competition between the two couplings. The temperature dependence of the ratio P/Θ also influences the temperature dependence of the pitch p or $q=2\pi/p$

$$q=\frac{\Lambda}{K_3}+\frac{\mu P}{K_3\Theta}+\frac{d\Theta^2}{K_3}\,, \tag{2}$$

as it follows from the equilibrium condition. In order to describe the anomalous temperature dependence [8] of p, the second term on the right-hand side of Eq. (2) which is proportional to P/Θ has to be of opposite sign to the first and the third term. Consequently, the wave vector q gets smaller on lowering the temperature from T_c (due to the increase of P/Θ), reaches a minimum, and at still lower temperatures increases monotonically due to the Lifshitz term of higher order (the d term). The helical period $p=2\pi/q$ thus increases sharply on lowering the temperature from T_c, assumes a maximum about 1 K below T_c, and then decreases on lowering the temperature farther. The minimum in q and thus the maximum in p are a result of the competition between the increase in P/Θ and the chiral d term, which tends to lower the pitch p. The temperature where the ratio P/Θ increases is thus intimately related to the temperature where p assumes its maximal value. The above properties of the ratio P/Θ and the pitch p in the absence of external fields are important since they influence the temperature dependences of the critical magnetic and electric field and thus the reentrance of the Sm-C^* phase.

The regions of stability of the high-temperature Sm-A, the modulated Sm-C^*, and the homogeneously tilted Sm-C phase in an external magnetic or electric field are presented usually on the phase diagram in dependence on the temperature and on the field strength. The phase diagrams in an external magnetic and electric field have been investigated theoretically as early as 1977 by Michelson *et al.* [19] in the frame of the Landau model which is equivalent to the Pikin-Indenbom model [12]. In an external magnetic field below the Lifshitz point the Sm-$C^*\leftrightarrow$Sm-C transition was found to be first order. In an external electric field the Sm-$C^*\leftrightarrow$Sm-C transition was established to be continuous of an instability type at temperatures just below T_c, while at a lower temperature a tricritical point was found.

Further theoretical investigation by Benguigui and Jacobs [20] based on a rigorous numerical analysis of the Pikin-Indenbom model showed that this model has to be extended in order to explain the reentrance of the Sm-C^* phase in the magnetic field. The Jacobs-Benguigui model, which is a special example of the Landau model defined by Eq. (1) for $\Omega=0$ and $\eta=0$, leads to the reentrance of the Sm-C^* phase, if one goes beyond the constant amplitude approximation (CAA) (i.e., where only the phase of the order parameter is allowed to vary in space) and treats the problem numerically. However, the Jacobs-Benguigui model is able to describe adequately only such compounds which show a monotonic decrease of the pitch p on lowering the temperature. This model is thus inappropriate in the case of DOBAMBC and similar compounds with anomalous temperature dependence of the pitch p. This model is also unable to explain the observed [3] relationship between the critical magnetic field H_c and the pitch p, $H_c \propto 1/p$. Later on the Sm-$C^* \leftrightarrow$Sm-C transition was investigated [21] within the extended model (1). The authors chose the model parameters in the best way to fit the measured critical field H_c in DOBAMBC in dependence on the temperature and found an agreement. The same values of the model parameters were shown to fit well also the measured temperature dependence of the pitch p. Moreover, the comparison between the rigorous numerical results and the results within the CAA showed that the observed relationship $H_c \propto 1/p$ is a result of the validity of the CAA, which was shown theoretically to be valid at all temperatures except for $T_c - T \lesssim 0.1$ K. The model introduced through Eq. (1) thus proved to be successful also in explaining the behavior of ferroelectric liquid crystals in an external magnetic field.

As for the theoretical investigation of the reentrant Sm-C^* phase in the external electric field, recently Benguigui and Jacobs [22] made a classification of the temperature dependence of the critical magnetic and electric field with respect to all possible temperature dependences of the pitch. Their analysis and a comparison to experimental data in DOBAMBC yielded a relationship between the reentrance of the Sm-C^* phase and the anomalous temperature dependence of the pitch p. In the following we show that in DOBAMBC the nonmonotonic temperature dependence of the critical magnetic as well as the critical electric field are a consequence of the same physical mechanism which also causes the anomalous temperature dependence of the pitch. The observed relationship between the critical electric field, the pitch p, the tilt Θ, and the polarization P, which is a result of the CAA, is shown to be valid even close to T_c similar to the magnetic-field case [21]. Some new results and some comments about Ref. [22] are presented in order to make an understanding of the behavior in external fields more clear.

The measured [3] temperature dependence of the critical magnetic field in DOBAMBC has been fitted [21] with the rigorous numerical results obtained in the frame of the extended model (1). In the same model, which can be characterized by six dimensionless parameters, the temperature dependence of the critical electric field E_c is calculated for *the same values of the parameters* as it has been done in the magnetic-field case [21]. The result is shown in Fig. 1, where also the measured [11] values of E_c are depicted. If we compare Fig. 1 of Ref. [21] and Fig. 1 of the present paper, we see that both critical fields (H_c and E_c) in DOBAMBC assume the minima at $T_c - T \approx 0.5$ K, i.e., at the temperature where the pitch p is maximal. Thus the reentrance of the Sm-C^* phase in

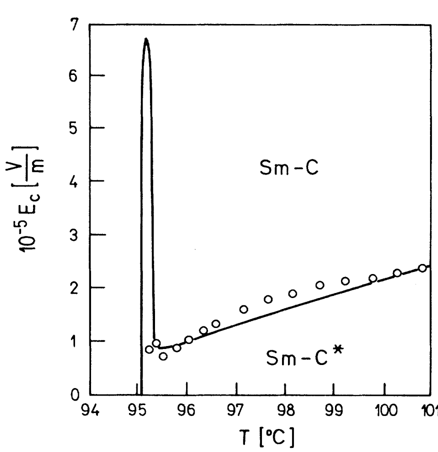

FIG. 1. The experimentally determined critical field in DOBAMBC is presented in dependence on the temperature (circles). The critical field obtained on the basis of the extended model is shown as a solid line. The model parameters, used in the calculation, have the same values as in the magnetic-field case [21].

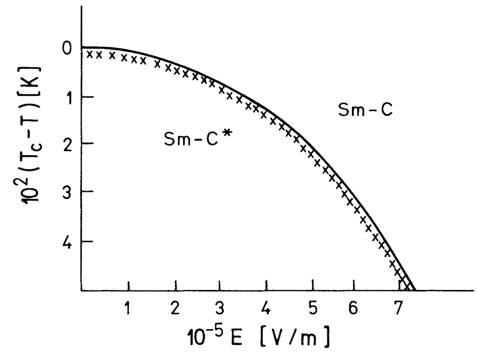

FIG. 2. Two critical-field lines, the line obtained numerically by a rigorous treatment (solid line) of the problem and the CAA result (crosses), are compared in the frame of the extended model.

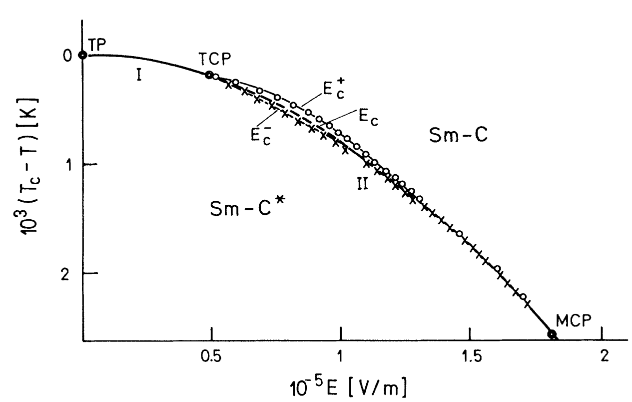

FIG. 3. The phase diagram in an external electric field determined within the Pikin-Indenbom model is presented at temperatures just below T_c. The critical-field line E_c and the two stability lines E_c^- and E_c^+ of the Sm-C and Sm-C^* phases, respectively, join together in the two critical points, the tri- and the multicritical point.

the magnetic as well as in the electric field has the same physical origin as the anomalous behavior of the pitch p.

The measured values of E_c (see Fig. 1) have been taken from Ref. [11] where an alternative method of determining E_c has been introduced. This experimental method is based on the assumption that the CAA relationship which has been used already by Meyer *et al.* [1]

$$E_c^{CAA} = \left(\frac{\pi}{4}\right)^2 \frac{K_3\Theta^2 q^2}{P} \quad (3)$$

is valid. Results of this method agree well [11] with results of the direct E_c measurements [10] at temperatures $T_c - T < 6$ K, which supports the validity of Eq. (3). As shown in Fig. 2, our rigorous numerical results for E_c also agree with the CAA relationship (3), even very close to T_c, which is consistent with experimental findings.

Within the Jacobs-Benguigui model ($\Omega = 0$ and $\eta = 0$) a CAA relationship $E_c^{CAA} \propto \Theta q^2$ [compare Eq. (4) in Ref. [22]] analogous to Eq. (3) can be found. This relationship is a special example of Eq. (3) and is valid only for compounds where the ratio P/Θ is temperature independent, i.e., where there is no anomalous behavior of the ratio P/Θ and the pitch p. The test of the experimental validity of the relationship $E_c \propto \Theta q^2$ made in Ref. [22] thus brings no surprise: if the temperature regime $T_c - T < 1$ K, where the quantities P/Θ and p behave anomalously, is omitted, then the Jacobs-Benguigui model can be applied and consequently the above relationship becomes valid.

Just below T_c the invariants of higher order (the c, d, Ω, and η terms) in the free energy density (1) do not influence the critical-field line. For DOBAMBC we find the Pikin-Indenbom model ($c = 0$, $d = 0$, $\Omega = 0$, and $\eta = 0$) to be valid at temperatures $T_c - T < 0.1$ K. In this temperature regime the Sm-C^*↔Sm-C transition changes from an instability to a nucleation type on lowering the temperature from T_c. There are two critical points on the critical-field line. Between them the transition is first order. Figure 3 shows the positions of the two critical points in DOBAMBC, together with two stability limits of the Sm-C^* and Sm-C phases, respectively, as determined numerically. It can be seen that the hysteresis due to the discontinuous transition is quite small.

To conclude, we have studied the problem of the reentrant Sm-C^* phase in external fields for a typical ferroelectric liquid-crystalline compound DOBAMBC, which is the only compound with all necessary experimental data needed to determine the model parameters. The reentrance of the Sm-C^* phase in the magnetic and electric field is shown to have the same physical origin as the anomalous temperature dependence of the pitch p. Both critical-field lines can be reasonably well described within the extended Landau model, using the *same values of the model parameters.* According to the Landau model the Sm-C^*↔Sm-C transition in an electric field is predicted to be continuous of the nucleation type for temperatures $T_c - T > 2.5$ mK. This seems to disagree with the observed hysteresis in critical-field measurements, but it can be explained by taking into account the dynamical behavior of phase solitons [21], as it is discussed in detail elsewhere [23].

[1] R.B. Meyer, L. Liébert, L. Strzelecki, and P. Keller, J. Phys. (Paris) Lett. **36**, L69 (1975).
[2] M. Yamashita, in *Solitons in Liquid Crystals*, edited by L. Lam and J. Prost (Springer-Verlag, New York, 1992), Chap. 10.
[3] I. Muševič, B. Žekš, R. Blinc, Th. Rasing, and P. Wyder, Phys. Rev. Lett. **48**, 192 (1982); R. Blinc, I. Muševič, B. Žekš, and A. Seppen, Phys. Scr. **T35**, 38 (1991).
[4] Ph. Martinot-Lagarde, R. Duke, and G. Durand, Mol. Cryst. Liq. Cryst. **75**, 249 (1981).
[5] H. Takezoe, K. Kondo, A. Fukuda, and E. Kuze, Jpn. J. Appl. Phys. **21**, L627 (1982).
[6] S.A. Rozański, and W. Kuczyński, Chem. Phys. Lett. **105**, 104 (1984).
[7] H. Takezoe, K. Kondo, K. Miyasato, S. Abe, T. Tsuchiya, A. Fukuda, and E. Kuze, Ferroelectrics **58**, 55 (1984).
[8] I. Muševič, B. Žekš, R. Blinc, L. Jansen, A. Seppen, and P. Wyder, Ferroelectrics **58**, 71 (1984).
[9] A. Fukuda and E. Kuze, Jpn. J. Appl. Phys. **22**, L43 (1983).
[10] S. Dumrongrattana and C.C. Huang, J. Phys. (Paris) **47**, 2117 (1986).
[11] A. Levstik, Z. Kutnjak, B. Žekš, S. Dumrongrattana, and C.C. Huang, J. Phys. II **1**, 797 (1991).
[12] V.L. Indenbom, S.A. Pikin, and E.B. Loginov, Kristallografiya **21**, 1093 (1976) [Sov. Phys. Crystallogr. **21**, 632 (1976)]; S.A. Pikin and V.L. Indenbom, Ferroelectrics **20**, 151 (1978).
[13] B. Žekš, Mol. Cryst. Liq. Cryst. **114**, 259 (1984).
[14] S. Dumrongrattana and C.C. Huang, Phys. Rev. Lett. **56**, 5 (1986).
[15] T. Carlsson, B. Žekš, C. Filipič, A. Levstik, and R. Blinc, Mol. Cryst. Liq. Cryst. **163**, 11 (1988).
[16] B. Žekš, T. Carlsson, C. Filipič, and B. Urbanc, Ferroelectrics **84**, 3 (1988).
[17] S. Dumrongrattana and C. C. Huang, Phys. Rev. Lett. **56**, 464 (1986).
[18] B. Urbanc and B. Žekš, Liq. Cryst. **5**, 1075 (1989); B. Žekš and B. Urbanc, Ferroelectrics **113**, 151 (1991).
[19] A. Michelson, Phys. Rev. Lett. **39**, 464 (1977); Phys. Rev. B **16**, 577 (1977); A. Michelson and D. Cabib, J. Phys. (Paris) Lett. **38**, L321 (1977); A. Michelson, L. Benguigui, and D. Cabib, Phys. Rev. A **16**, 394 (1977).
[20] L. Benguigui and A.E. Jacobs, Ferroelectrics **84**, 379 (1988); A.E. Jacobs and L. Benguigui, Phys. Rev. A **39**, 3622 (1989).
[21] B. Kutnjak-Urbanc and B. Žekš, Phys. Rev. E **48**, 455 (1993).
[22] L. Benguigui and A.E. Jacobs, Phys. Rev. E **49**, 4221 (1994).
[23] B. Kutnjak-Urbanc and B. Žekš (unpublished).