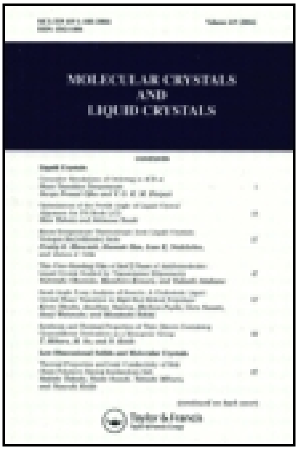

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LIFSHITZ–LIKE BEHAVIOUR IN FERROELECTRIC LIQUID CRYSTALS

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Abstract In order to explain the anomalous behaviour of the critical magnetic field and the helical pitch in the vicinity of the λ–line and the Lifshitz point in the ferroelectric liquid crystal DOBAMBC a model involving not only chiral but also non–chiral biquadratic coupling between the polarization and the tilt has been proposed. The model predicts an "S – like" dependence of the modulation wave vector close to the smectic C* – smectic A transition. High temperature resolution measurements of the helical pitch and the intensity of the diffraction sattelites indeed support the proposed model and seem to show that the pitch is finite at T_c. In such a case the Lifshitz field H_L is finite too.

I. INTRODUCTION

The chiral ferroelectric smectic C* phase (SmC*) represents a spatially modulated structure[1]. The tilt of the long molecular axis from the normal to the smectic layers and the in-plane spontaneous polarization precess as one goes from one smectic layer to another resulting in a periodic helicoidal modulation of the refractive index. An aligned sample thus acts as a one dimensional birefringent diffraction grating with the grating constant equal to the pitch of the helix (p). The helix disappears in strong enough magnetic[2] or electric[3] fields and the tilt and polarization directions become uniform in space. The unwinding transition between the modulated C* and the uniform C phase is to a certain extent analogous to the incommensurate – commensurate transition in crystalline ferroelectrics[4]. At higher temperatures the tilt vanishes and the system makes a transition to the disordered smectic A (SmA) phase. The triple point between disordered Sm A, the homogeneously ordered Sm C and the modulated Sm C* phase represents a Lifshitz point[5]. The properties of ferroelectric liquid crystals are far from being well understood. The temperature dependence of the critical magnetic field H_c for the unwinding of the helix for p–decyloxbenzilidene–p–amino–2–methyl–buthyl cinamate (DOBAMBC) has been determined[2] by light scattering and dielectric measurements (Fig. 1) and does not agree with theoretical predictions. H_c decreases slowly with T at low temperatures,

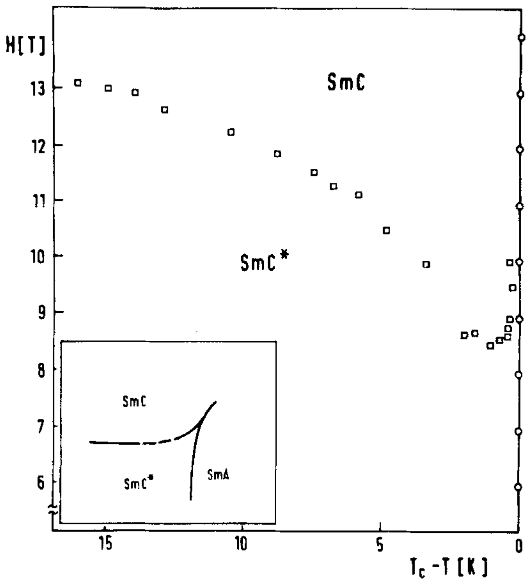

FIGURE 1. Phase diagram of chiral DOBAMBC in an external magnetic field applied at right angles to the helical axis. The inset shows the theoretically predicted phase diagram arround the Lifshitz point.

reaches a minimum about 1 K below T_c and then increases rapidly to experimentally inaccessible values whereas it should be almost temperature independent according to simple theoretical models[5]. The anomaly in H_c is similar to the anomaly in the temperature dependence of the helical pitch (Fig. 2) which should as well be temperature independent according to the simple Landau theory[2]. The pitch p slowly increases with increasing temperature, reaches a maximum at approximately the same temperature where H_c has a minimum and then sharply decreases with increasing temperature[6–8]. The underlying mechanism for the anomalies in p (T) and H_c (T) seems to be the same and an understanding of the p (T) anomaly is needed in order to understand the temperature dependence of the critical field H_c. There exist several different theoretical models for the anomalous temperature dependence of the pitch[9–12] but the situation is still not completely

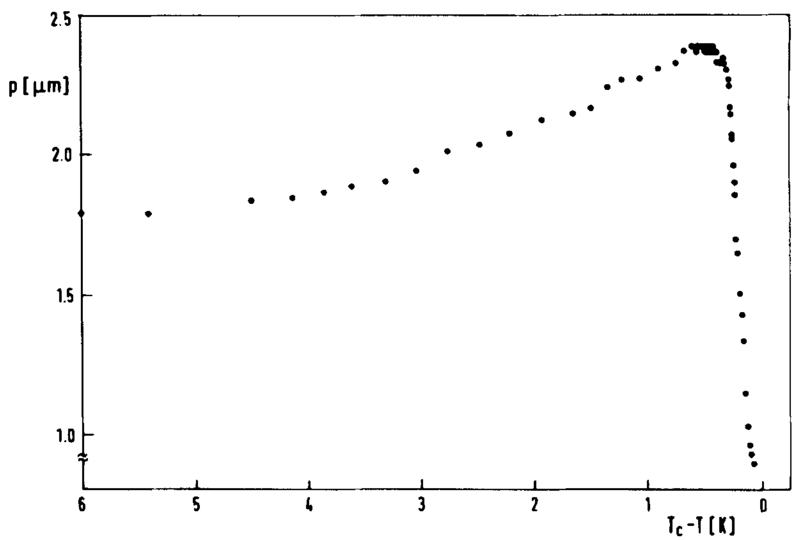

FIGURE 2: Temperature dependence of the pitch of the helix in DOBAMBC in a relatively broad temperature interval.

understood. The predicted temperature dependences differ only close to T_c where the existing data are rather scarce. Therefore we decided to remeasure the temperature and magnetic field dependence of the helical pitch in DOBAMBC as well as the T–dependence of the intensities of the higher order diffraction sattelites with special *emphasis on the region close to* T_c *and to compare the results with* theoretical predictions.

II. THEORY

A. Classical Landau model:

a) The Landau free energy density describing the Sm A – Sm C* transition is usually expressed as[1]

$$g(z) = g_o + \frac{1}{2} a (\xi_1^2 + \xi_2^2) + \frac{1}{4} b (\xi_1^2 + \xi_2^2)^2 - \Lambda (\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz})$$
$$+ \frac{1}{2} K_{33} [(\frac{d\xi_1}{dz})^2 + (\frac{d\xi_2}{dz})^2] + \frac{1}{2\epsilon} (P_x^2 + P_y^2) -$$
$$- \mu (P_x \frac{d\xi_1}{dz} + P_y \frac{d\xi_2}{dz})$$
$$+ C (P_x \xi_2 - P_y \xi_1), \qquad (1)$$

where

$$\xi_1 = n_z n_x \approx \vartheta \cos\varphi, \qquad \xi_2 = n_z n_y \approx \vartheta \sin\varphi, \qquad (2a)$$
$$P_x = - P \sin\varphi \qquad P_y = P \cos\varphi, \qquad (2b)$$

represent the order parameters of the Sm A – Sm C* transition. Here ϑ is the tilt angle and $\varphi = \varphi(z)$ the azimuthal angle determining the orientation of the molecular director $\bar{n} = (n_x, n_y, n_z)$ with respect to the normal $\bar{\nu} = (0,0,1)$ to the smectic layers. P_x and P_y are the components of the in–plane polarization, $a = \alpha(T - T_o)$, $b > 0$, K_{33} is the elastic modulus, Λ the coefficient of the Lifshitz term responsible for the modulation and μ and C are the coefficients of the "flexo" – and "piezo" – electric coupling between the tilt and the polarization.

In the plane wave limit $\varphi = q_c z$ and minimization of $F = \frac{1}{L}\int_0^L g(z)\,dz$ with respect to ϑ, P and q_c yields the Sm A – SmC* transition temperature T_c, the temperature dependence of the tilt angle and the pitch of the helix as well as the spontaneous polarization P:

$$\vartheta = \sqrt{\frac{\alpha}{b}(T_c - T)}, \tag{3a}$$

$$T_c = T_o + \frac{1}{\alpha}[\epsilon C^2 + (K_{33} - \epsilon\mu^2)\, q_c^2], \tag{3b}$$

$$p = \frac{2\pi}{q_c} = 2\pi\frac{K_{33} - \epsilon\mu^2}{\Lambda + \epsilon\mu C} = 2\pi\frac{\widetilde{K}_{33}}{\widetilde{\Lambda}}, \tag{3c}$$

$$P = \epsilon(\mu q_c + C)\vartheta. \tag{3d}$$

Within this model the pitch of the helix p does not depend on temperature in contrast to experiments. The spontaneous polarization P is proportional to the tilt.

b) In the presence of a magnetic field H applied in a direction x perpendicular to the helical axis, a term

$$\Delta g_H = -\frac{1}{2}\chi_a H^2 n_x^2, \tag{4}$$

has to be added to the free energy density (1). The magnetic field tends to align the molecules because of their magnetic anisotropy $\chi_a = \chi_\parallel - \chi_\perp$ and deforms the helix. For $H > H_c$ the modulated structure is not stable and the system makes a transition into a homogeneously tilted SmC phase. The SmC*, SmA and SmC phases coexist at the Lifshitz point which is – according to Michelson – given by

$$T_L = T_o + 4\widetilde{K}_{33}\, q_c^2/\alpha, \tag{5a}$$

$$H_L = 2\widetilde{\Lambda}(K_{33}\,\chi_a)^{-1/2}. \tag{5b}$$

The "plane wave" modulation model is valid only close to the λ line separating the SmA and SmC* phases. For low enough temperatures the free energy F has to be minimized with respect to φ (z) leading to a sine–Gordon equation

$$\frac{d^2\varphi}{dz^2} = \left(\frac{\chi_a H^2}{\tilde{K}_{33}}\right) \sin(2\varphi) , \tag{6}$$

which admits non–linear phase soliton solutions for $H \neq 0$. The critical field H_c for the unwinding of the helix is here 21 % smaller than the Lifshitz field H_L

$$H_c = (\pi/4)\, H_L , \tag{7}$$

but is again T–independent in contrast to the experiments.

c) In the presence of an electric field E applied perpendicular to the helical axis, a term

$$\Delta g_E = - E_y P_y , \tag{8a}$$

has to be added to the free energy density. The dielectric response to such a homogeneous electric field is given by

$$\chi = \frac{\epsilon^2 C^2}{\alpha (T - T_c) + \tilde{K}_{33} q_c^2} + \epsilon , \quad T > T_c , \tag{8b}$$

$$\chi = \frac{1}{2} \epsilon^2 C^2 \left[\frac{1}{2\alpha (T_c - T) + \tilde{K}_{33} q_c^2} + \frac{1}{\tilde{K}_{33} q_c^2}\right] + \epsilon , \quad T < T_c . \tag{8c}$$

The dielectric susceptibility contains a soft mode contribution above T_c and a soft mode as well as a Goldstone mode contribution – proportional to the square of the helical pitch – below T_c.
The Goldstone mode contribution does not depend on temperature, whereas the soft mode contribution is T – dependent and should give rise to a peak in χ at T_c. Experimentally a peak in χ is observed below and not at T_c.
A comparison between the predictions of the classical Landau model

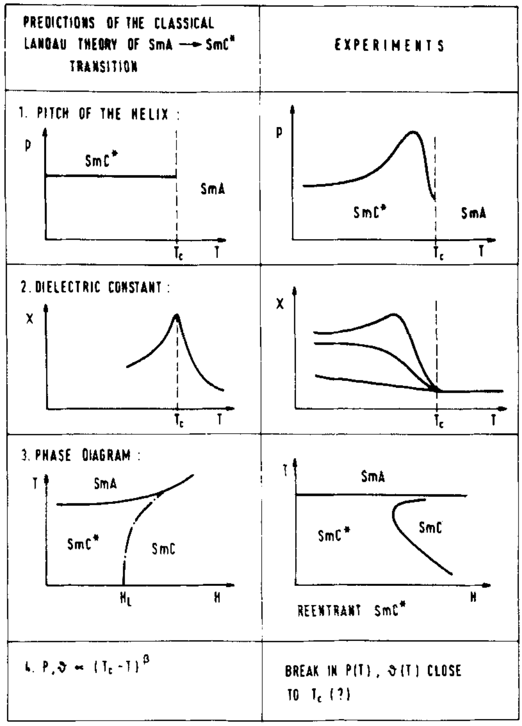

FIGURE 3. Comparison between the predictions of the "classical" Landau theory of the SmA – SmC* transition (with "piezo–electric" and "flexo – electric" coupling between the tilt and the polarization) and the experimental results.

and the experimental results is presented in Fig. 3. The discrepancies can be summarized as follows:

1. the pitch of the helix is not constant, but shows an anomalous T – dependence,
2. the peak in the dielectric constant is not at T_c but below T_c. It does n o t coincide with the peak in the pitch,
3. the phase diagram $T_c = T_c(H)$ shows a reentrant SmC* phase and a T – dependent critical field H_c in contrast to the theory,
4. according to unpublished data from our laboratory the T – dependence of the polarization and the tilt seem to show a change in the slope close to T_c not predicted by the theory.

The anomalies in the critical magnetic field and the pitch of the helix are related to each other as H_c is inversely proportional to the pitch of the undisturbed helix:

$$H_c = \frac{1}{2} \pi q_c \sqrt{K_{33}/\chi_a} \, . \tag{9}$$

We may thus hope that a model describing properly the T – dependence of the pitch will also describe the phase diagram $T_c = T_c(H)$. If q_c is finite at T_c then H_c and H_L are finite too and there indeed exists a Lifshitz point in chiral SmC* systems in a finite magnetic field.

B. Alternative models

There exist at least four different modifications of the above model introduced to explain the anomalous temperature dependence of the pitch and H_c close to T_c:

(i) Critical fluctuations [9],

(ii) Anomalous flexo–electric coefficient [10],

(iii) Unwinding via defects[(11)],

(iv) Non–chiral biquadratic coupling [12] between the polarization and the tilt.

Whereas it can be shown[13] that critical fluctuations do not affect $\langle d\varphi/dz \rangle$, the other three models can not be excluded at present. Here we shall discuss only the last of the above models.

C. Non–chiral biquadratic coupling between the tilt and the polarization

The difference in the transition temperatures $T_c - T_o$ between chiral DOBAMBC and a racemic mixture[1,14] is small: $T_c - T_o \leqslant 10^{-1}$ K. This suggests that in the free energy density expansion (1) all chiral terms are small as compared to non–chiral ones. NMR measurements further show[15] that in the low temperature smectic phasses there is no appreciable difference in the orientational ordering of the molecules in a direction transverse to their long axes between chiral and non–chiral systems except perhaps in the vicinity of T_c. Since P describes the transverse polar orientational ordering which is present only in chiral systems whereas P^2 describes the transverse quadrupolar ordering which is present in both chiral and non–chiral systems the NMR results can only be described by adding a term inducing a quadrupolar orientational ordering to the free energy expansion (1). Such a term is the non–chiral biquadratic P—ϑ coupling.

We must thus add to the usual free energy density expansion (1) the lowest order non–chiral terms:

$$g_a = -\frac{1}{2}\Omega\,(P_x\,\xi_2 - P_y\,\xi_1)^2 + \frac{1}{4}\eta\,(P_x^2 + P_y^2)^2. \tag{10}$$

The biquadratic Ω term is non–chiral and large and induces a transverse quadrupolar ordering as observed in NMR[15]. The last term has been added to stabilize the system ($\eta > 0$).
We should as well include a higher order term (12, 1c)

$$g_b = -d\,(\xi_1^2 + \xi_2^2)\,(\xi_1\frac{d\xi_2}{dz} - \xi_2\frac{d\xi_1}{dz}), \tag{11}$$

which is equivalent to replacing Λ by $\Lambda + \vartheta^2$ thus yielding a ϑ-–dependent pitch

$$p/p_c = \Lambda/(\Lambda + d\vartheta^2), \tag{12}$$

where p_c is the value of the pitch at $\vartheta = 0$. i.e. at $T = T_c$. For $T < T_c$ expression (12) well describes the slow increase of p with increasing temperature for $T < T_c - 1$ K.

A direct consequence of the addition of the biquadratic $P-\vartheta$ coupling term (10) is a highly non–linear $P(\vartheta)$ dependence which influences the temperature dependence of the pitch through the flexoelectric coupling close to T_c. Let us now investigate the effect of this term in some details.

The total free energy density can be now rewritten as

$$g_T = g_o + \frac{1}{2}a\vartheta^2 + \frac{1}{4}b\vartheta^4 - \Lambda q\vartheta^2 + \frac{1}{2}K_{33}q^2\vartheta^2 - dq\vartheta^4 +$$

$$+ \frac{1}{2\epsilon}P^2 - \mu q\vartheta P - C\vartheta P - \frac{1}{2}\Omega\vartheta^2P^2 + \frac{1}{4}\eta P^4. \quad (13)$$

The minimization of expression (13) with respect to ϑ, P and q can be performed only numerically. Some approximate analytical expressions can be obtained nevertheless. The form of the "potential" for P

$$V(P,\vartheta,q) = \frac{1}{2}\left(\frac{1}{\epsilon} - \Omega\vartheta^2\right)P^2 + \frac{1}{4}\eta P^4 - (\mu q + C)\vartheta P, \quad (12)$$

depends strongly on the magnitude of the tilt angle ϑ. It has a single minimum for

$$\text{(i)}\ \vartheta < \vartheta_o = 1/\sqrt{\epsilon\Omega}, \quad (13a)$$

whereas it is of the double minimum type for

$$\text{(ii)}\ \vartheta > \vartheta_o = 1/\sqrt{\epsilon\Omega}. \quad (13b)$$

In the limit $C + \mu q \to +0$ we get for

$$\text{(i)}\ \vartheta < \vartheta_o,\ P_o = 0, \quad (14a)$$

whereas

$$\text{(ii)}\ \vartheta > \vartheta_o,\ P_o^2 = \frac{\Omega}{\eta}(\vartheta^2 - \vartheta_o^2). \quad (14b)$$

Inserting the above values into g_T and minimizing with respect to q one finds in the limit where chiral terms have only a small effect on ϑ:

$$q = \frac{\Lambda}{K_{33}} [1 + \frac{d\alpha}{\Lambda b} (T_c - T)], \quad \vartheta < \vartheta_o , \tag{15a}$$

and

$$\vartheta^2 = \frac{\alpha}{b} (T_c - T) , \quad \vartheta < \vartheta_o . \tag{15b}$$

For $\vartheta > \vartheta_o$, on the other hand, one finds:

$$\vartheta^2 = \frac{\alpha (T_c' - T)}{b - \Omega^2/\eta} , \quad \vartheta > \vartheta_o , \tag{16a}$$

$$P^2 = \frac{\Omega}{\eta (b - \Omega^2/\eta)} \cdot \alpha (T_c'' - T) , \quad \vartheta > \vartheta_o , \tag{16b}$$

$$q = \frac{\Lambda}{K_{33}} [1 + \frac{d . \alpha}{\Lambda (b - \Omega^2/\eta)} (T_c' - T) + \frac{\mu}{\Lambda} \sqrt{\frac{\Omega}{\eta}} \sqrt{\frac{T_c'' - T}{T_c' - T}}] , \quad \vartheta > \vartheta_o , \tag{16c}$$

where

$$T_c' = T_c - \frac{\Omega^2}{\alpha \eta} \vartheta_o^2 < T_c , \tag{17a}$$

$$T_c'' = T_c - \frac{b}{\alpha} \vartheta_o^2 < T_c' . \tag{17b}$$

The resulting temperature dependences of the tilt ϑ, the helical pitch p and the polarization P are illustrated in figures 4, 5 and 6 for two sets of parameters. The characteristic features of the above results are:

(i) the normalized value of the pitch increases with increasing temperature, reaches a maximum and then decreases close to T_c reaching a finite value ($p/p_o = 1$) at T_c.

(ii) The temperature dependences of ϑ and P should exhibit an S – like behaviour with a characteristic change in the slope close to T_c. A finite value of C will make the change in the slope less sharp than shown in figures 4 and 6 but it should be still there.

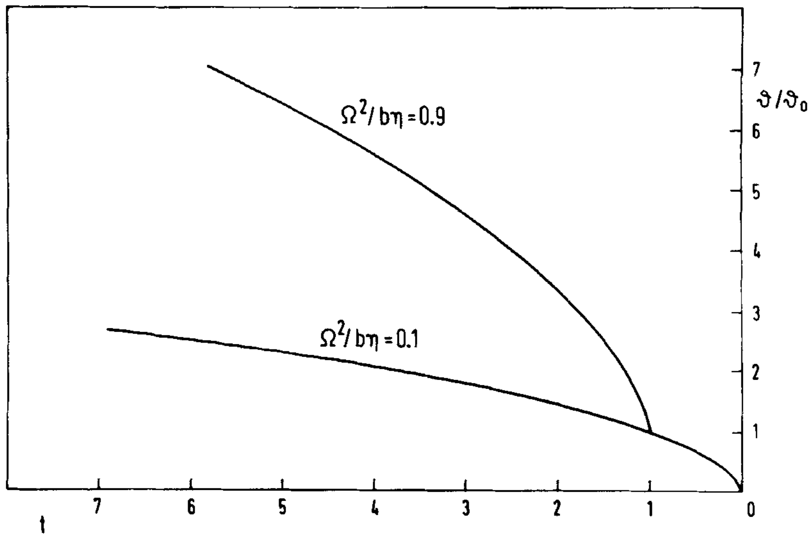

FIGURE 4. Temperature dependence of the normalized tilt angle close to T_c according to model C with $t = (\alpha/b\vartheta_o^2)(T_c - T)$.

The "S—like" T—dependence of the spontaneous polarization results in a maximum in the dielectric constant b e l o w and not at T_c.

These last features should enable one to discriminate between the different theoretical models if experimental data with a high enough temperature resolution are available.

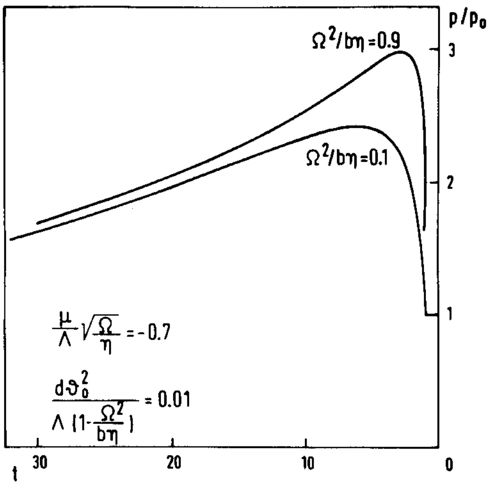

FIGURE 5. Temperature dependence of the normalized helical pitch close to T_c according to model C with $t = (\alpha/b\theta_o^2)(T_c - T)$.

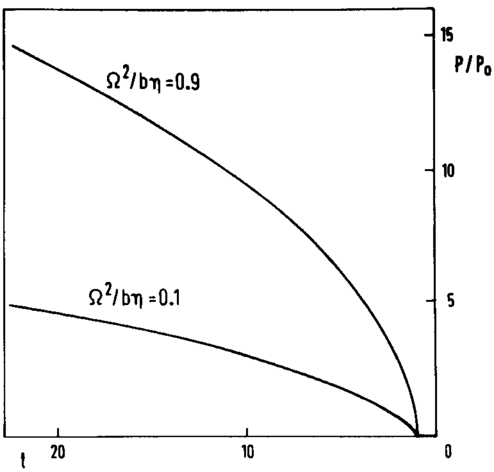

FIGURE 6. Temperature dependence of the spontaneous in plane polarization close to T_c according to model C with $t = (\alpha/b\theta_o^2)(T_c - T)$ and $P_o = (\Omega\,\theta_o^2/\eta)^{1/2}$.

III. EXPERIMENTS AND DISCUSSION

The pitch of the chiral SmC* phase was measured with laser light diffraction on 75 μm thick monodomain samples aligned in a high magnetic field. A two stage temperature controller and a double shielded system were used in experiments, giving $\pm$ 1 mK temperature stability. All measurements were done at constant light intensity in order to prevent uncontrolled sample heating due to light absorption in the liquid crystal layer.

The samples were prepared by sandwiching the liquid crystal between the two carefully cleaned glass plates and sealed with an inert epoxy. The sample was heated into the isotropic phase and an ordered Sm A phase with smectic layers perpendicular to the glass surface was obtained by cooling the sample through the isotropic — Sm A phase transition in the presence of a 10 T magnetic field applied parallel to the glass surface. The maximum cooling rate for the sample alignment was 1 K/h. Once in the Sm A phase, the field was switched off and the sample was slowly cooled through Sm A — SmC* transition. The temperature dependence of the pitch was measured in the direction of increasing temperature with 647.1 nm and 476.2 nm laser wavelengths. The transition temperature T_c was determined with stronger 647.1 nm laser wavelength. Because of experimental limitation of maximum diffraction angle in the measurements, the pitch could not be measured in the range $T_c - T < 100$ mK with 647.1 nm wavelength and $T_c - T < 50$ mK with 476.2 nm wavelength because of poor signal to noise ratio. Due to finite width of diffraction peaks, the last measurement where the tail of the first order intensity distribution was visible was taken as the transition temperature T_c.

The temperature dependence of the intensity of the far field diffraction patterns is presented in Fig. 7. For the general case, the intensities of the various diffraction sattelites can be calculated only numerically. Close to T_c, where $\vartheta^2 \rightarrow 0$, the sample becomes optical-

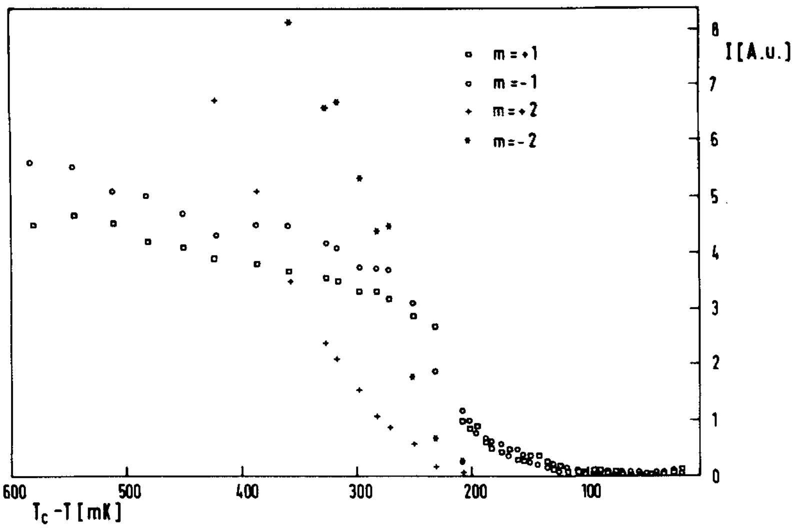

FIGURE 7. Temperature dependence of the intensities of the first and the second order diffraction sattelites close to T_c .

ly thin and the Raman — Nath approximation for a phase grating can be used. In such a case the intensities of the various sattelites are proportional to the squares of the Bessel functions of order m and argument ϕ

$$I_m \propto |J_m(\phi)|^2,$$

where for m = 1, for instance, $\phi = \frac{1}{2} k \Delta n \vartheta^2$ with Δn standing for the optical anisotropy in the index of refraction and k for the wave vector of light. Since k and Δn are temperature independent and $J_1(\phi) \propto \phi$ for $\phi \ll 1$ the fourth root of I_1 should reflect the temperature dependence of ϑ for $T \rightarrow T_c$. Such a plot is presented in Fig. 8 and indeed seems to show two regions in the $\vartheta = \vartheta(T_c - T)$

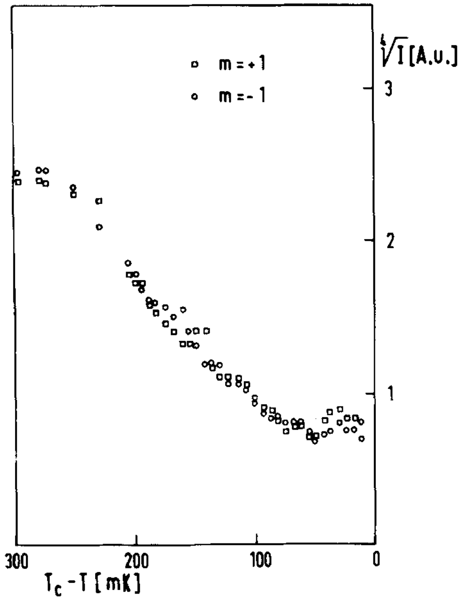

FIGURE 8. Temperature dependence of the fourth root of the intensity of the first order diffraction sattelites which should reflect the temperature dependence of the tilt angle ϑ.

dependences as predicted by the theoretical model presented in chapter III.

The temperature dependence of the pitch very near the SmC* — SmA transition is presented in Fig. 9, whereas the results for a broader temperature range are given in Fig. 2. The pitch is increasing with temperature up to $T = T_c - 600$ mK, reaches a constant value in the range 600 mK $> T_c - T >$ 300 mK and then decreases with increasing temperature to a finite non—zero value as $T \rightarrow T_c$. The modulation wave vector — as shown in the insert to Fig. 9 — shows an "S — like" behaviour close to T_c as predicted by the model involving non—chiral biquadratic coupling between the tilt and the polarization.

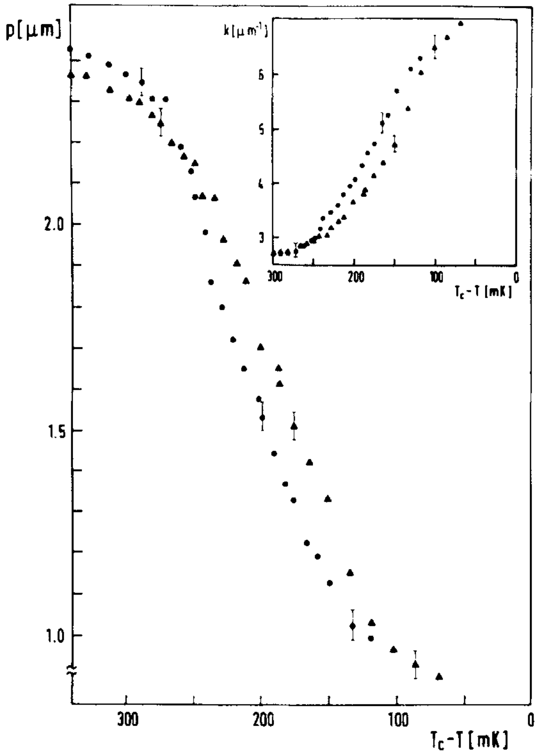

FIGURE 9. Temperature dependence of the pitch of the helix close to T_c. The inset shows the temperature dependence of the modulation wave vector.

The fact that there is no divergence in q_c close to T_c allows us to conclude—via expression (9) — that H_c and H_L are finite too. Thus a Lifshitz point seems to exist after all in the T vs. H phase diagram of chiral SmC* systems.

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