Phase Diagram of a Ferroelectric Chiral Smectic Liquid Crystal near the Lifshitz Point

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The phase diagram of chiral smectic p-decyloxybenzilidene-p'-amino-2-methylbutyl cinnamate in an external magnetic field parallel to the smectic layers has been determined by dielectric and optical measurements up to 14.5 T. The data indicate the existence of a Lifshitz point between the disordered smectic-A, the modulated smectic-C^*, and the homogeneously ordered smectic-C phases. A reentrant C^* phase has been found above 8.5 T. The critical field for the unwinding of the helix becomes extremely large as the λ line is approached.

The Lifshitz point[1] is that point on a line of second-order phase transitions where an instability occurs in wave vector ($\vec{k}$) space. It represents a special case of a triple point between a disordered, a homogeneously ordered ($\vec{k} = 0$), and a modulated ($\vec{k} \neq 0$) ordered phase. The experimental data on the behavior of physical systems near the Lifshitz point are rather scarce.[2]

Some time ago Michelson[3] predicted that a Lifshitz point exists in the T-H phase diagram of chiral smectic liquid crystals if the magnetic field H is applied parallel to the smectic layers. In this Letter we present the first observation of the phase diagram of the chiral ferroelectric[4] smectic liquid crystal p-decyloxybenzilidene-p'-amino-2-methylbutyl cinnamate (DOBAMBC) in an external magnetic field. The data suggest that a Lifshitz point indeed exists between the disordered smectic-A, the helicoidally ordered smectic-C^*, and the homogeneously ordered smectic-C phases.

The observed T_c-H phase diagram in a magnetic field up to 14.5 T is shown in Fig. 1. The A-C^* line—which is within ±50 mK H independent—was found to be of second order whereas the C-C^* transition line is of first order close to the λ line. The discontinuity in k becomes smaller as the Lifshitz point is approached along the C^*-C boundary. Above $H = 8.5$ T the C-C^* line changes its direction so that a reentrant smectic-C^* phase was found.

In order to determine the phase boundaries we measured the temperature and magnetic field dependence of the in-plane component of the dielectric constant ϵ and of the pitch $2\pi/k$ of the

smectic-C^* helix in 75-μm-thick monodomain samples. Optically flat glass plates with transparent SnO_2 electrodes on the inner side have been used to allow for simultaneous dielectric
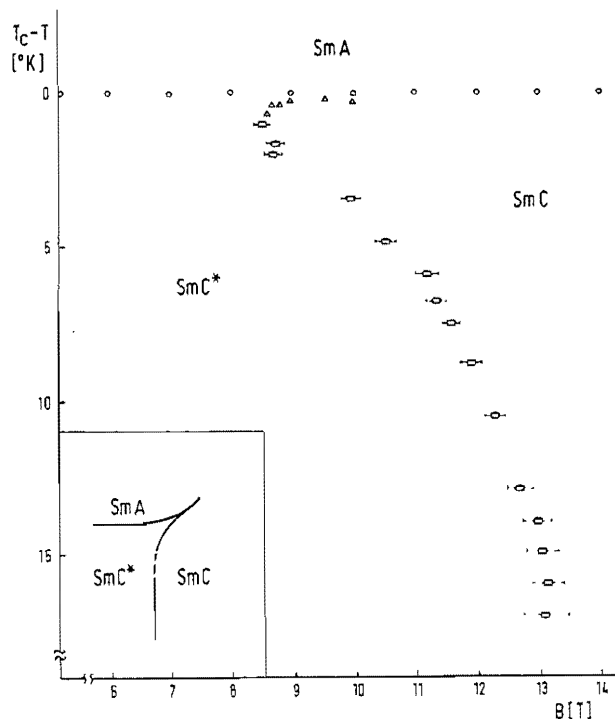

FIG. 1. Phase diagram of chiral DOBAMBC near the smectic-A–smectic-C^*–smectic-C triple point. The magnetic field H is applied parallel to the smectic layers. The inset shows the phase diagram predicted by Ref. 3 whereas the low-temperature part of the C^*-C phase boundary line has been evaluated from the sine-Gordon equation following de Gennes (Ref. 6).

and optical measurements. The monodomain samples were prepared by slowly (1 °C/h) cooling the system through the isotropic–smectic-A transition in a magnetic field of 10 T which was parallel to the sample walls. In this way all molecules orient parallel to the walls of the cell. After that the magnetic field H was decreased to a very small value, the system was slowly cooled into the smectic-C^* phase, and the sample was rotated for 90° so that $\vec{k} \perp \vec{H} \perp \vec{E}$, where $\vec{k}/k$ is the axis of the helix and $\vec{E}$ the ac electric field ($\nu = 20$ Hz) used for measurements of the in-plane component of the dielectric constant ϵ. The C-C^* phase boundary and the critical magnetic field H_c for the unwinding of the smectic-C^* helix was determined by measuring $\epsilon = \epsilon(H)$ at $T = \text{const}$. The sweep 0–14.5 T was made in about 10 min. The A-C^* boundary was determined by measuring $\epsilon = \epsilon(T)$ at $H = \text{const}$. The results have been corrected for the observed decrease of T_c because of sample aging (~50 mK/h). The optical

measurements were performed by automatically recording the intensity of the diffracted He-Ne laser light on a screen behind the sample. The monodomain sample acted as a one-dimensional diffraction grating and the intensity of the scattered light was measured with a Si phototransistor. The diffraction maxima were found to be very sharp at $T < T_c - 0.5$ K, whereas at $T - T_c$ the diffracted intensity in the smectic-C^* phase drastically decreases because of the decrease of the molecular tilt. Just below the λ line the dependence $k = k(H)$ was measured at $T = \text{const}$ (Fig. 2) whereas at several selected values of H, $k = k(T)$ was studied (Fig. 3). The sample was realigned after every C^*-C transition passage.

Before discussing the above results let us first recall[5,6] some theoretical predictions of the relevant models proposed so far. The nonequilibrium free energy density above the A-C^* transition can be—in the presence of an external magnetic field H which is perpendicular to the direction of the
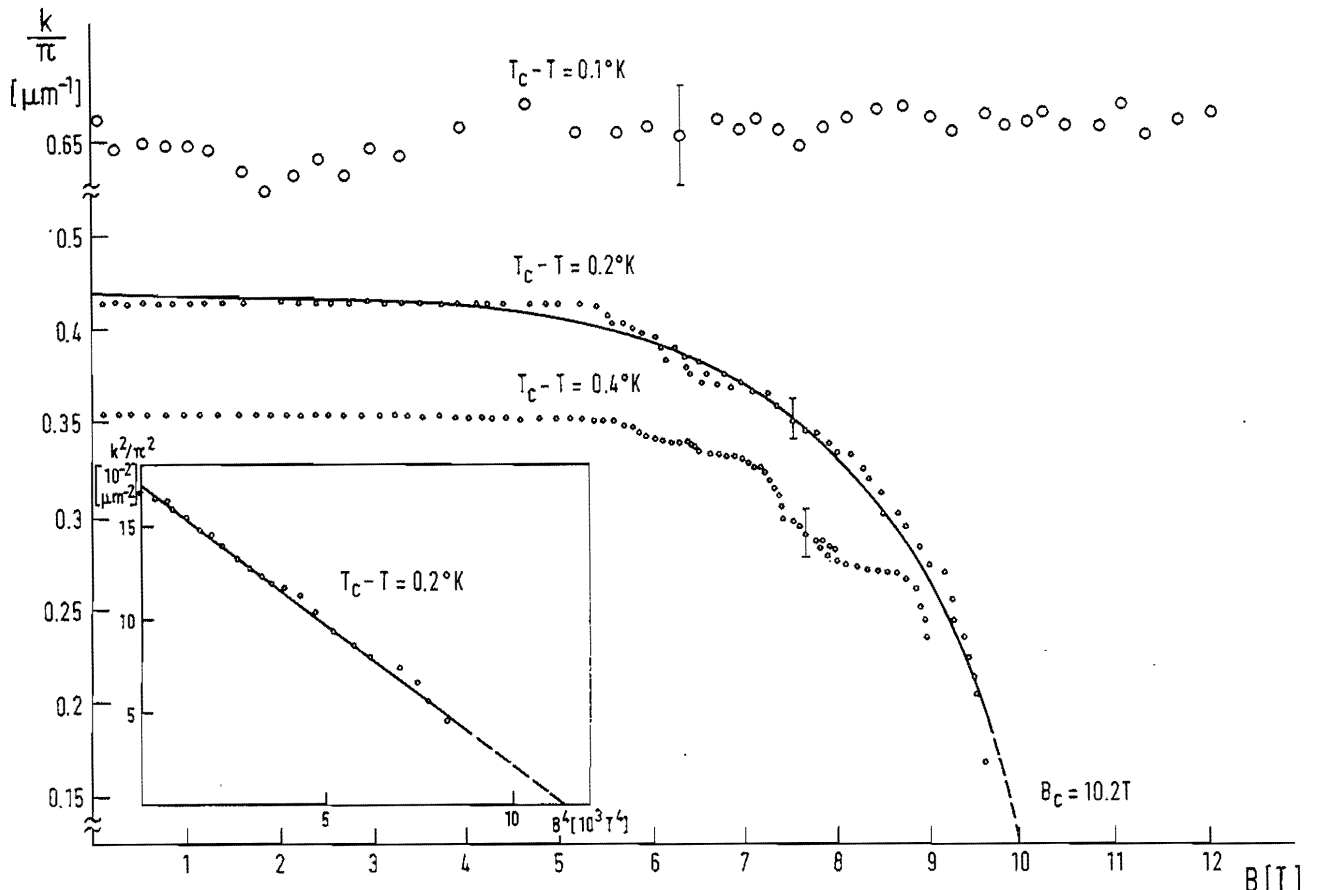

FIG. 2. Magnetic field dependence of the inverse pitch at different temperatures. The solid line shows the fit of the data at $T_c - T = 0.2$ K by Eq. (6) with $H_L = 10.2$ T. The inset shows the k^2 vs H^4 plot at $T_c - T = 0.2$ K used for the determination of the "apparent" Lifshitz field H_L.

pitch—expressed[3,5] as

$$g = \tfrac{1}{2}a\left(n_x{}^2 + n_y{}^2\right) + \tfrac{1}{4}b\left(n_x{}^2 + n_y{}^2\right)^2 + \Lambda\left(n_x\frac{dn_y}{dz} - n_y\frac{dn_x}{dz}\right) + \tfrac{1}{2}K_{33}\left[\left(\frac{dn_x}{dz}\right)^2 + \left(\frac{dn_y}{dz}\right)^2\right] - \tfrac{1}{2}\chi_a H^2 n_x{}^2, \tag{1}$$

where the diamagnetic anisotropy χ_a is positive for DOBAMBC; the coefficient $a = \alpha(T - T_0)$ varies linearly with temperature whereas all other coefficients are assumed to be temperature independent. K_{33} is the elastic modulus and $b > 0$. The presence of the Lifshitz term, Λ, leads in the smectic-C^* phase—in the absence of a strong enough magnetic field—to a helicoidal precession of the molecular director $\bar{n} = (n_x, n_y, n_z)$ around the normal $(n_x = n_y = 0, \ n_z = 1)$ to the smectic layers. Below the A-C^* transition temperature

$$T_c = T_0 + \alpha^{-1}\Lambda^2/K_{33} = T_0 + \Delta T, \tag{2}$$

the molecular tilt is nonzero $(n_x \neq 0, \ n_y \neq 0)$ and the helical precession of the tilt in the z direction is characterized for $H = 0$ by a temperature-independent wave vector

$$k_0 = \Lambda/K_{33}. \tag{3}$$

In the presence of a magnetic field H which is smaller than the Lifshitz field H_L the A-C^* λ line is determined[3] by

$$T_\lambda = T_0 + \Delta T\left(1 + H^2/H_L{}^2\right)^2, \quad H < H_L, \tag{4a}$$

whereas the A-C line is given[3] by

$$T = T_0 + 4\Delta T\left(H/H_L\right)^2, \quad H > H_L, \tag{4b}$$

where

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

The magnetic field dependence of the wave vector of the C^* helix is along the λ line obtained[3] as

$$k_\lambda{}^2(H) = k_0{}^2\left(1 - H^4/H_L{}^4\right), \quad H < H_L, \tag{6}$$

whereas $k_\lambda = 0$ for $H > H_L$. The analysis of Michelson[3] further showed that the k line (i.e., the C^*-C phase boundary line) approaches the A-C^* λ line tangentially at the Lifshitz point and that the C^*-C transition is of first order. The "plane wave" modulation model of the C^* phase used by Michelson[3] is valid only close to the λ line. For low enough temperatures one can use for the analysis of the C^*-C phase-boundary line the approach used by de Gennes[6] in studying the unwinding of the cholesteric helix in a transverse magnetic field. Introducing

$$n_x = A\cos\varphi(z), \ n_y = A\sin\varphi(z), \tag{7}$$

making the constant-amplitude approximation, $A = \text{const}$, and minimizing the free energy F

$= L^{-1}\int_0^L g(z)\,dz$ with respect to φ, one finds $\varphi = \varphi(z)$ as a solution of the sine-Gordon equation

$$d^2\varphi/dz^2 = \left(\chi_a H^2 K_{33}/2\Lambda^2\right)\sin(2\varphi) \tag{8}$$

which admits nonlinear 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 given by Eq. (5),

$$H_c/H_L = \pi/4 = 0.79, \tag{9}$$

but is again T independent. The C^*-C transition is now a second-order one and the C^*-C phase boundary should be vertical, i.e., parallel to the T axis. The constant-amplitude approximation should fail close to the λ line. It can be shown

FIG. 3. Temperature dependence of the inverse pitch at different applied magnetic fields.

to be valid as long as

$$T_0 - T \gg 2\Lambda^2/\alpha K_{33} = 2\Delta T, \qquad (10)$$

where ΔT is smaller[7] than 50 mK. The phase diagram expected on the basis of the above considerations is sketched in the inset to Fig. 1.

Though qualitatively correct the above model is too simple to describe the experimental data quantitatively. Neither the existence of a reentrant C^* phase above 8.5 T nor the fact that H_L is bigger than $1.27 H_c$ can be accounted for by the above model considerations.

When k is measured as a function of H at constant T (Fig. 2) the discontinuity in k at the C^*-C transition decreases with increasing T, i.e., on approaching the Lifshitz point as predicted. The $k = k(H)$ curve at $T_c - T = 0.2$ K can be reasonably well (Fig. 2) described by Eq. (6) with $H_L = 10.2$ T as determined by a plot of k^2 vs H^4. From the measurement at $T_c - T = 0.1$ K, however, one sees that in fact H_L is bigger than 14 T. One can thus say the system behaves in the way predicted by Michelson up to $T_c - T \simeq 0.2$ K but that for $T_c - T < 0.2$ the critical field for the unwinding of the helix strongly increases with increasing temperature.

As can be seen from Fig. 3 the above model even fails to describe the T dependence of k at $H = 0$. Whereas k indeed varies relatively little with temperature over most of the C^* phase it

increases drastically on approaching the C^*-A transition when $T_c - T < 0.2$ K.

We believe that fluctuations in the vicinity of T_c result in a renormalization of the constants of our model which thus become temperature dependent—$K_{33} = K_{33}(T)$, $\Lambda = \Lambda(T)$—resulting in a temperature dependence of the pitch of the helix: $k(T) = \Lambda(T)/K_{33}(T)$. The experimental data show that the minimum in $H_c = H_c(T)$ occurs at the same temperature as the minimum in $k = k(T)$. Since to a first approximation H_c seems to be proportional to $\sqrt{k(T)}$ we conclude that $\Lambda \approx$ const and that it is K_{33} which is proportional to the pitch (i.e., k^{-1}) and thus becomes strongly temperature dependent close to T_c.

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