Physical Realization of a Lifshitz Point in Liquid Crystals

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A theoretically based proposal of a concrete physical realization of a Lifshitz point is given for the first time. This point should occur on the $\mathcal{H}$-T diagram of a chiral liquid crystal exhibiting a second-order transition between the smectic phases A and helicoidal C ($\mathcal{H}$ is a magnetic field parallel to the smectic layers). The phase diagram near this point is shown to be similar to the one obtained in the case of uniaxial magnetization.

The Lifshitz point, introduced recently by Hornreich, Luban, and Shtrikman,[1] has become a subject of growing interest.[2-4] To get some notion of a Lifshitz point, consider a Landau-Ginzburg free-energy functional

$$F=\int[A\mu^2+B\mu^4+\sum_{i=x,y,z}\alpha_i(\nabla_i\mu)^2+\ldots]d^3r, \qquad (1)$$

where μ is a scalar order parameter, and the expansion coefficients A, B, and α_i depend on temperature T and some external parameter $\mathcal{H}$. The line $T_0(\mathcal{H})$ on the $\mathcal{H}$-T diagram defined by the equation $A(\mathcal{H}, T)=0$ corresponds to order-disorder phase transitions of second order so long as $\alpha_i>0$ on this line. One can imagine a situation where, on moving along the line $T_0(\mathcal{H})$, one reaches a point $(\mathcal{H}_L, T_L)$ where one of the α_i's (say α_z) vanishes and further becomes negative. This point is called the Lifshitz point. The continuation of the line $T_0(\mathcal{H})$ into the region $\alpha_z<0$ does not correspond to any phase transitions. Instead, it enters a new phase, a *modulated* ordered phase, characterized by a wave vector $\vec{k}_0=\vec{k}_0(\mathcal{H}, T)$, which increases *continuously* from $\vec{k}_0=0$ at $(\mathcal{H}_L, T_L)$. The Lifshitz point is thus a special case of triple point between the disordered, uniformly ordered, and modulated ordered phases. The critical behavior in the vicinity of a Lifshitz point was studied by Hornreich, Luban, and Shtrikman,[1] and the thermodynamics of the system in this vicinity by the present author.[3] However, no definite, theoretically based prediction of a concrete physical realization of Lifshitz point has been presented hitherto. In Refs. 1–3, the possibility of a Lifshitz point rests on an *assumption* that the above parameter α_z (or its counterpart in the particular expansion of F) *can* change sign under certain controllable variation of external conditions (pressure, material composition, external fields). The suggestions made in Refs. 3 and 4 concerning possible realizations of Lifshitz point are just empirical conjectures, and it is unclear whether these should be realizations of a Lifshitz point or merely of some triple point between the three above-mentioned phases. In this Letter, I make a *theoretically based* proposal of a physical realization of Lifshitz point. The system considered here is a smectic liquid crystal composed of chiral molecules and exhibiting a second-order transition between the smectic-A and helicoidal smectic-C phases. Such systems have recently been synthesized.[5] The external parameter $\mathcal{H}$ in question is a uniform magnetic field parallel to the smectic layers. I will show that the $\mathcal{H}$-T diagram of such a system exhibits a Lifshitz point between three smectic phases: A, C, and modulated C (the latter will henceforth be named the C^* phase).

As is known, the smectic-A to smectic-C phase transition can be described in terms of de Gennes's order parameter[6] $\psi=n_x+in_y$, where n_x and n_y are the x and y components of the nematic director $\hat{n}$ (it is assumed that the z axis is normal to the smectic layers). The same order parameter can be used to describe the smectic-A to smectic-C^* phase transition, the C^* phase being helicoidal in the absence of external fields. Since only spatial variation of ψ along the z direction is relevant, the Landau-Ginzburg expansion of the free energy $F(\psi)$ can be written in the form[7]

$$F=\int[K_1|\psi|^2+iK_2(\psi\partial\psi^*/\partial z-\psi^*\partial\psi/\partial z)+K_3|\partial\psi/\partial z|^2+K_4|\psi|^4]d^3r. \qquad (2)$$

As usual in the Landau theory,[8] the coefficient K_1 is assumed to depend linearly on temperature: $K_1=a(T-\theta)$, and the rest of the coefficients in (2) are assumed to be practically independent of T. In order to determine the transition temperature T_c and the type of ordering below T_c, one has to consider the "harmonic" term in F, i.e., that part of F which is a quadratic functional of ψ. Introducing the Fourier expansion $\psi(z)=\sum_k\psi_k e^{ikz}$, one can present the "harmonic" part of F in the form

$$F^{(2)}=V\sum_k\alpha_k|\psi_k|^2, \qquad (3)$$

where V is the volume of the system, and

$$\alpha_k = K_1 + 2K_2k + K_3k^2. \quad (4)$$

The "soft mode" of the phase transition in question is associated with the minimum of the "frequency band" a_k. This minimum occurs at $k = k_c = -K_2/K_3$ and equals $a_{k_c} = K_1 - K_2^2/K_3$. Accordingly, the ordering below T_c is described by $\psi(z) = \psi_{k_c}\exp(ik_c z)$, which corresponds to the helicoidal precession of the nematic director $\hat{n}$ about the z axis, with a wave number k_c. The temperature T_c is determined from the equation $a_{k_c} = 0$ and equals

$$T_c = \theta + a^{-1}K_2^2/K_3. \quad (5)$$

For a racemic mixture of two isomers of the same chiral molecule, $K_2 = 0$.[7] Then, on the assumption that the rest of the coefficients in (2) are only slightly affected by the change from the chiral to the racemic version of the same compound, one may identify θ with the A-C phase-transition temperature for the racemic version. In the presence of magnetic field $\vec{\mathcal{H}}$, one has to add the term[6] $-\frac{1}{2}\chi(\vec{\mathcal{H}}\cdot\hat{n})^2$ to the free-energy density, where $\chi = \chi_\parallel - \chi_\perp$; $\chi_\parallel$ is the susceptibility along the long molecular axis (per unit volume) and $\chi_\perp$ in the perpendicular direction. Assuming for definiteness that $\vec{\mathcal{H}}$ is parallel to the x axis, one obtains, instead of (3),

$$F^{(2)} = V\sum_k[(a_k - \tfrac{1}{4}\chi\mathcal{H}^2)|\psi_k|^2 - \tfrac{1}{8}\chi\mathcal{H}^2(\psi_k\psi_{-k} + \text{c.c.})]. \quad (6)$$

Thus, the magnetic field introduces coupling between the modes ψ_k and ψ_{-k}. The expression for $F^{(2)}$ can be diagonalized by the following canonical transformation to new variables μ_k and ν_k:

$$\psi_k = b_k\mu_k - c_k\nu_k, \quad \psi_k{}^* = c_k\mu_k + b_k\nu_k, \quad (7)$$

where

$$b_k = [\tfrac{1}{2} - k(4k^2 + \chi^2\mathcal{H}^4/16K_2^2)^{-1/2}]^{1/2}, \quad (8a)$$

$$c_k = \frac{[\tfrac{1}{2} + k(4k^2 + \chi^2\mathcal{H}^4/16K_2^2)^{-1/2}]^{1/2}\chi}{|\chi|}, \quad (8b)$$

$$\mu_{-k} = (\chi/|\chi|)\mu_k{}^*, \quad \nu_{-k} = -(\chi/|\chi|)\nu_k{}^*. \quad (9)$$

The expression for $F^{(2)}$ becomes

$$F^{(2)} = \tfrac{1}{2}V\sum_k(A_k{}^-|\mu_k|^2 + A_k{}^+|\nu_k|^2), \quad (10)$$

where

$$A_k{}^\pm = K_1 + K_3k^2 - \tfrac{1}{4}\chi\mathcal{H}^2 \pm \tfrac{1}{4}(\chi^2\mathcal{H}^4 + 64K_2^2k^2)^{1/2}. \quad (11)$$

Now, the "soft mode" of the phase transition is associated with the minimum $A_{\min}$ of $A_k{}^-$, which is the lower of the two "frequency bands," $A_k{}^+$ and $A_k{}^-$. If $\mathcal{H} < \mathcal{H}_L$, where

$$\mathcal{H}_L = (8K_2^2/K_3|\chi|)^{1/2} = [8a(T_c - \theta)/|\chi|]^{1/2}, \quad (12)$$

then $A_{\min}$ occurs at

$$k_0 = k_c(1 - \mathcal{H}^4/\mathcal{H}_L{}^4)^2 \quad (13)$$

and equals

$$A_{k_0}{}^- = K_1 - K_2^2K_3^{-1}(1 + \chi\mathcal{H}^2/|\chi|\mathcal{H}_L{}^2)^2. \quad (14)$$

If $\mathcal{H} > \mathcal{H}_L$, then $A_{\min}$ occurs at $k = 0$ and equals

$$A_0{}^- = K_1 - \tfrac{1}{4}(\chi + |\chi|)\mathcal{H}^2. \quad (15)$$

The temperature T_λ of the second-order transition from the smectic-A phase to a lower-symmetry phase is determined from the equation $A_{\min} = 0$ and

$$T_\lambda = \begin{cases} \theta + \Delta T(1 + \chi\mathcal{H}^2/|\chi|\mathcal{H}_L{}^2)^2, & \mathcal{H} \leq \mathcal{H}_L \\ \theta + 2(1 + \chi/|\chi|)\Delta T\mathcal{H}^2/\mathcal{H}_L{}^2, & \mathcal{H} \geq \mathcal{H}_L, \end{cases} \quad (16)$$

where $\Delta T \equiv T_c - \theta$. At $\mathcal{H} = 0$, $k_0 = k_c$ and $T_\lambda = T_c$, as should be expected. For $\mathcal{H} < \mathcal{H}_L$, the freezing of the "soft mode" μ_{k_0} below T_λ leads to a smectic-C^* phase, with a modulated ordering of long molecular axes. According to (7), this ordering is described by

$$\psi(z) = b_{k_0}\mu_{k_0}\exp(ik_0z) + c_{k_0}\mu_{k_0}{}^*\exp(-ik_0z), \quad (17)$$

or, in terms of n_x, n_y, by

$$n_x(z) = (b_{k_0} + c_k)|\mu_{k_0}|\cos(k_0z + \varphi),$$
$$n_y(z) = (b_{k_0} - c_{k_0})|\mu_{k_0}|\sin(k_0z + \varphi), \quad (18)$$

where φ is an arbitrary constant, and

$$b_{k_0} = (1/\sqrt{2})(1 - k_0/k_c)^{1/2},$$
$$c_{k_0} = (1/\sqrt{2})(1 + k_0/k_c)^{1/2}\chi/|\chi|. \quad (19)$$

Equations (18) show that the projection of $\hat{n}$ on the smectic layer varies in space as a static eliptically polarized wave with the wave vector $\vec{k}_0 = k_0\hat{z}$. As $\mathcal{H} \to 0$, $k_0 \to k_c$ and this wave tends to a circularly polarized (i.e., helicoidal) one; as $\mathcal{H} \to \mathcal{H}_L - 0$, $k_0 \to 0$, and this wave tends to a linearly polarized one.

For $\mathcal{H} > \mathcal{H}_L$, the second-order transition from the A phase leads to the ordinary (uniform) smectic-C phase. In view of (16), the A-C transition temperature $T_0 \equiv T_\lambda(\mathcal{H} > \mathcal{H}_L)$ grows with $\mathcal{H}$ if $\chi > 0$ and is independent of $\mathcal{H}$ if $\chi < 0$ (see Fig. 1). According to Eqs. (8) and (9), if $\chi > 0$, then μ_0 is real, and below T_0 one finds $n_x = \mu_0/\sqrt{2}$, $n_y = 0$; if $\chi < 0$, μ_0 is imaginary, and below T_0 one obtains

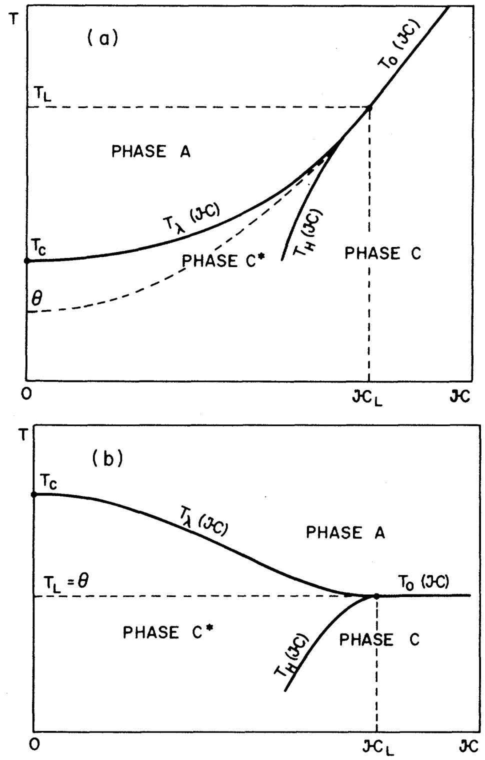

FIG. 1. $\mathcal{H}$-T diagram exhibiting a Lifshitz point $(\mathcal{H}_L, T_L)$ between the smectic-A, -C, and -C^* phases: (a) for $\chi > 0$, (b) for $\chi < 0$.

$n_x = 0$, $n_y = |\mu_0|/\sqrt{2}$. This means that for $\chi > 0$ the plane of the tilt of the molecules is parallel to $\vec{\mathcal{H}} = \mathcal{H}\hat{x}$, and for $\chi < 0$ it is perpendicular to $\vec{\mathcal{H}}$, as should be expected.

It follows from the above discussion that the point $(\mathcal{H}_L, T_L)$, where $T_L \equiv T_\lambda(\mathcal{H}_L)$, is indeed a Lifshitz point between the smectic-A, -C, and -C^* phases. In order to determine the order of the C-C^* phase transition and the shape of the C-C^* transition line near $(\mathcal{H}_L, T_L)$, let us write down the expansion of F near this point. Since only long-wave modes μ_k are essential in the critical behavior of the system in the vicinity of $(\mathcal{H}_L, T_L)$, it is sufficient to retain only the contribution of these modes to F. Then, omitting the terms with ν_k in (10), and expanding A_k^- to fourth order in k, one obtains

$$F^{(2)} = \tfrac{1}{2} V \textstyle\sum_k (A_0^- + \alpha k^2 + \beta k^4) |\mu_k|^2, \qquad (20)$$

where

$$\alpha = K_3 - 8K_2^2/|\chi|\mathcal{H}^2 \approx 2K_3(\mathcal{H}/\mathcal{H}_L - 1), \qquad (21)$$

$$\beta = 128/|\chi|^3\mathcal{H}_L^6. \qquad (22)$$

Similarly, substituting $\psi = \sum_k \psi_k e^{ikz}$, with ψ_k from Eq. (7), into the $|\psi|^4$ term in (2), and putting $b_k \simeq b_0 = 1/\sqrt{2}$, $c_k \simeq c_0 = \chi/\sqrt{2}|\chi|$, one obtains for the term of the fourth order in μ_k

$$F^{(4)} = \tfrac{1}{4} V K_4 \sum_{k,k',k''} \mu_k \mu_{k'} \mu_{k''} \mu_{-k-k'-k''}. \qquad (23)$$

Now, introducing an "effective order parameter"

$$\mu(z) = \textstyle\sum_k \mu_k e^{ikz}, \qquad (24)$$

one can present $F = F^{(2)} + F^{(4)}$ in the form

$$F = \frac{1}{2}\int \left[A_0\mu^2 + \alpha\left(\frac{\partial\mu}{\partial z}\right)^2 + \beta\left(\frac{\partial^2\mu}{\partial z^2}\right)^2 + \frac{1}{2}K_4\mu^4\right] d^3r. \qquad (25)$$

Expansion (25) is similar to the expansion of F in the vicinity of the Lifshitz point in the case of uniaxial magnetization, as discussed in a previous work (Ref. 3, paper I). (Observe that, though the original order parameter $\psi = n_x + in_y$ is a two-component one, the "effective order parameter," μ, associated with the Lifshitz point is *one-component*.) Hence the results of that work can be applied here straightforwardly. It follows that the smectic-C–smectic-C^* phase transition in question must be first order. The line $T_H(\mathcal{H})$ of this transition lies in the region $\mathcal{H} < \mathcal{H}_L$ and its *tangent* to the line $T_\lambda(\mathcal{H})$ at the point $(\mathcal{H}_L, T_L)$. The $\mathcal{H}$-T diagrams in question for $\chi > 0$ and $\chi < 0$ are shown in Fig. 1.

According to Eq. (13), the modulation wave number k_0 decreases with the growth of $\mathcal{H}$ (unwinding of the spiral) until the value of $\mathcal{H}$ reaches the boundary of the C^* phase, where k_0 changes abruptly to zero. This resembles the unwinding of the smectic-C^* in an electric field.[9] However, apart from some common features, the behavior of the C^* phase in an electric field should differ considerably from that in a magnetic field, because in the former case this behavior is governed mainly by ferroelectric coupling[5] linear in the field, whereas in the latter case by diamagnetic coupling quadratic in the field.

As was shown by Meyer *et al.*,[5] the systems in question have the following remarkable property: When the molecules in a layer become tilted, the layer acquires a nonzero electrical polarization normal to the plane of the tilt. It follows that the predicted formation of the smectic-C phase in the presence of $\vec{\mathcal{H}}$ must be accompanied by a certain uniform bulk polarization $\vec{P}$. If $\chi > 0$, then $\vec{P} \perp \vec{\mathcal{H}}$, and if $\chi < 0$, then $\vec{P} \,||\, \vec{\mathcal{H}}$. It should be of great interest ot detect this "magnetoelectric" effect experimentally.

The experimental observability of the above $\mathcal{H}$-

T diagram depends on the magnitudes of ΔT and $\mathcal{H}_L$; in particular, the Lifshitz field $\mathcal{H}_L$ should be accessible. According to Ref. 5, $\Delta T \sim 1°C$. Unfortunately, $\mathcal{H}_L$ cannot be estimated so long as the magnitude of α in (12) is unknown. However, $\mathcal{H}_L$ can be made arbitrarily small by preparing a sufficiently dilute solution of the chiral material in question in a nonchiral solvent. Indeed, $K_2 \to 0$ when the concentration of the chiral solute goes to zero.[7] Then, according to (12) also $\mathcal{H}_L \to 0$. Another method to decrease $\mathcal{H}_L$ is to prepare a mixture of two isomers of the same chiral molecule and to decrease the difference of their concentrations. Since $\Delta T \propto \mathcal{H}_L^2$, the required decrease of $\mathcal{H}_L$ to an available magnitude may (*not necessarily*) diminish ΔT so as to make it difficult to see the details of the phase diagram (Fig. 1 will undergo a strong contraction in the vertical direction). However, since the point $(\mathcal{H}_L, T_L)$ itself *can* be reached, it is possible to test the predictions of Ref. 1 concerning the critical behavior near this point.

Although the fluctuation corrections to the Landau theory affect the values of critical exponents, I expect that the existence of the Lifshitz point established above will be unaffected. Indeed, if one applies the renormalization-group method of Wilson,[10] one usually starts from the Landau free-energy functional (the Landau-Wilson Hamiltonian). The procedure of finding the actual symmetry-breaking order parameter (the "soft-mode") of the phase transition is then the same in the Landau theory.[11] Since *only* this procedure has been used above to establish the existence of the Lifshitz point, the result should not be affected by the renormalization.

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Energy Transport above T_c by Paramagnetic Magnons in Two-Dimensional Ferromagnetic Heisenberg Systems

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The thermal conductivity of the two-dimensional magnetic systems $(C_nH_{2n+1}NH_3)_2CuCl_4$ (with $n = 1,2$) has been measured from $0.12T_c$ to $2.5T_c$ in fields up to 6.5 T. We found a considerable heat transport by the magnetic system, both below and above T_c. Above T_c this heat transport can be attributed to magnonlike states which can exist well into the paramagnetic region in low-dimensionality systems.

The dynamics of fluctuations in both ordered and disordered spin systems are of considerable current interest. The existence of these spin fluctuations at temperatures far above the critical temperature T_c has been established by neutron scattering experiments for three-dimensional systems[1] as well as for systems of lower dimensionality.[2,3] But their functioning as agents of energy transport has never been observed before. In this Letter we report for the first time experimental evidence of the transport of thermal energy in the paramagnetic region by the spin system. This evidence follows from thermal-conductivity measurements in two-dimensional (2D) Heisenberg systems which show in the ordered phase a fractional magnon contribution of 90%—the largest yet observed—and above T_c a fractional magnetic contribution to the heat transport, ranging from 86% at T_c to a maximum of 95% at $T = 1.5T_c$, which can mainly be attributed to paramagnetic