Possibility of a Field-Induced Hexagonal Blue Phase in Cholesteric Liquid Crystals

R. M. Hornreich
Department of Electronics, Weizmann Institute of Science, Rehovot 76 100, Israel

and

M. Kugler
Department of Physics, Weizmann Institute of Science, Rehovot 76 100, Israel

and

S. Shtrikman
Department of Electronics, Weizmann Institute of Science, Rehovot 76 100, Israel
(Received 3 January 1985)

Phase diagrams of cholesteric liquid crystals in relatively weak electric or magnetic fields are calculated. In very weak fields the helicoidal-phase region grows at the expense of the cubic blue phases. A new phase, having a two-dimensional structure, is shown to appear at physically realizable chiralities for fields exceeding $E \simeq 70/(\Delta\epsilon)^{1/2}$ kV/cm and $H \simeq 20/(\Delta\chi)^{1/2}$ Oe, where $\Delta\epsilon$ ($\Delta\chi$) is the dielectric (diamagnetic) anisotropy. This structure exists between the disordered and cubic-blue-phase regions in the phase diagram.

PACS numbers: 61.30.Gd, 64.70.Ew

The cholesteric blue phases (BP) appear in a narrow temperature range immediately below the clearing point in a variety of chiral liquid-crystal systems.[1] An early attempt to explain their existence theoretically was made by Brazovskii and Dmitriev,[2] who suggested a two-dimensional (2D) hexagonal structure.[3] Such a structure, however, is not consistent with experimental results[1] (in particular, the absence of birefringence) and further theoretical work[4,5] showed that cubic ordering was the thermodynamically stable state.

We present arguments indicating that in the presence of an applied electric or magnetic field the 2D hexagonal structure may exist under appropriate conditions. This is done in the context of Landau theory, together with the assumption that the 2D phase occurs in relatively weak fields. In this regime, the order-parameter has essentially the same form as in the zero-field case. Finally, the weak-field assumption is shown to be justified.

Consider a uniform applied electric field **E** (in statvolts/cm). The Landau free-energy functional is[2,4-6]

$$F = V^{-1}\int d^3r\,[\tfrac{1}{2}(a\epsilon_{ij}^2 + c_1\epsilon_{ij,l}^2 + c_2\epsilon_{ij,i}\epsilon_{lj,l} - 2de_{ijl}\epsilon_{in}\epsilon_{jn,l}) - \beta\epsilon_{ij}\epsilon_{jl}\epsilon_{li} + \gamma(\epsilon_{ij}^2)^2] - (8\pi V)^{-1}E_iE_j\int d^3r\,\epsilon_{ij}, \quad (1)$$

where

$$\epsilon_{ij}(\mathbf{r}) = \epsilon_{ij}^d(\mathbf{r}) - \tfrac{1}{3}\mathrm{Tr}(\epsilon^d)\delta_{ij} \quad (2)$$

is the anisotropic part of the dielectric tensor $\epsilon_{ij}^d(\mathbf{r})$. In (1) a is proportional to a reduced temperature, c_1, c_2, d, β, and γ are temperature-independent parameters, $\epsilon_{ij,l} \equiv \partial\epsilon_{ij}/\partial x_l$, and summation on repeated indices is understood. Thermodynamic stability requires that c_1, γ, and $c_1 + \frac{2}{3}c_2$ all be greater than zero. For periodic structures

$$\epsilon_{ij}(\mathbf{r}) = \sum_{hkl} N^{-1/2}\epsilon_{ij}(\sigma)\exp[iq(hx+ky+lz)], \quad (3)$$

with $\sigma = h^2 + k^2 + l^2$ and N the multiplicity. Note that only the $h = k = l = 0$ Fourier component of $\epsilon_{ij}(\mathbf{r})$ contributes to the electric field energy term in (1) and that this term therefore vanishes for the case of cubic symmetry.

For the helicoidal C phase $\mathbf{E} = 0$ order parameter is[5]

$$[\epsilon_C(\mathbf{r})] = -\frac{1}{\sqrt{6}}\epsilon_0\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&2\end{pmatrix} + \frac{1}{2\sqrt{2}}\epsilon_2\left[e^{i(q_Cz+\psi)}\begin{pmatrix}1&i&0\\i&-1&0\\0&0&0\end{pmatrix} + \text{c.c.}\right], \quad (4)$$

where c.c. denotes complex conjugate. Our basic assumption is that this functional form of $[\epsilon_C(\mathbf{r})]$ is unchanged

in weak fields, with, however, ϵ_0 and ϵ_2 becoming **E** dependent. Denoting by $\epsilon_{\parallel}, \epsilon_{\perp}$ the dielectric constants parallel and perpendicular to the nematic axis in a fully aligned specimen gives

$$\epsilon_0 = (\epsilon_{\parallel} - \epsilon_{\perp})/\sqrt{6} = \Delta\epsilon/\sqrt{6}. \tag{5}$$

We consider $\Delta\epsilon > 0$ and partially minimize F by taking $\mathbf{E} = E\hat{i}_x$. Setting $\partial F/\partial q_C = 0$ yields $q_C = d/c_1$ and we scale F using

$$\epsilon_i = s\mu_i, \quad s = \beta/\sqrt{6}\gamma, \quad f = F/(\beta^4/36\gamma^3), \quad \tfrac{1}{4}t = (3\gamma/\beta^2)a,$$
$$\tfrac{1}{4}\xi_R^2 = (3\gamma/\beta^2)c_1, \quad \kappa = q_C\xi_R, \quad e = (3\gamma^2/4\pi\beta^3)^{1/2}E, \tag{6}$$

to obtain

$$f_C = \tfrac{1}{4}t\mu_0^2 + \tfrac{1}{4}(t-\kappa^2)\mu_2^2 + (\mu_0^3 - 3\mu_0\mu_2^2) + (\mu_0^2+\mu_2^2)^2 - \mu_0 e^2. \tag{7}$$

Setting $\partial f_C/\partial\mu_0 = \partial f_C/\partial\mu_2 = 0$ determines the equilibrium value of the order parameter for given t, κ, and e^2.

In our weak-field framework, the cubic BP free energies are **E** independent. We can therefore simply use results obtained elsewhere[5,7] for these phases. On the other hand, the free energy of the helicoidal phase is *lowered* in a weak electric field. Thus, an external field can change a cubic structure into a helicoidal one.

Consider now the 2D hexagonal structure. In the Brazovskii-Dmitriev model[2] only $q_C \neq 0$ Fourier components were included in $\epsilon_{ij}(\mathbf{r})$, in which case there can be no **E** dependence in the weak-field limit. However, there is, in fact, a symmetry-allowed $q = 0$ component in (3) whose tensor amplitude has its unique axis perpendicular to the 2D plane.[4,5] As before, we shall take the form of the order parameter to be identical to that for $\mathbf{E} = 0$. Upon adding the explicit external field term we obtain[5,8]

$$f_{Hm} = \tfrac{1}{4}t\mu_0^2 + \tfrac{1}{4}(t-\kappa^2)\mu_2^2 - \tfrac{27}{32}\mu_2^3 - \tfrac{3}{2}\mu_0\mu_2^2 - \mu_0^3 + \tfrac{233}{192}\mu_2^4 + \tfrac{9}{8}\mu_0\mu_2^3 + \tfrac{7}{2}\mu_0^2\mu_2^2 + \mu_0^4 - 2\mu_0 e^2. \tag{8}$$

The field **E** now lies parallel to the structure's unique axis and the order-parameter equilibrium value follows from $\partial f_{Hm}/\partial\mu_0 = \partial f_{Hm}/\partial\mu_2 = 0$.

In an external electric field the disordered phase becomes nematic and its free energy is given by

$$f_N = \tfrac{1}{4}t\mu^2 - \mu^3 + \mu^4 - 2\mu e^2. \tag{9}$$

In a weak electric field this has a minimum at $\mu \sim O(e^2)$ so that $f_N \sim O(e^4)$. Thus f_N is small.

Comparing (7) and (8), we see that free energy of the *Hm* phase is lowered more by an electric field than that of the helicoidal phase. This is the mechanism that stabilizes the *Hm* phase.

Upon minimization and comparison of the free energies of the different structures, the phase diagrams in Figs. 1 and 2 are obtained. In the first figure we give, for different values of e^2, the (κ,t)-plane phase diagram. We find that the 2D *Hm* phase is thermodynamically stable above $e_{\text{th}}^2(\kappa = 1.3) = 0.028$. This is shown from an alternative aspect in Fig. 2. Note that the *C*-phase Bragg back-reflection wavelength λ_C^{air} is related to our reduced variables by

$$\lambda_C^{\text{air}} = 4\pi n\xi_R/\kappa, \tag{10}$$

where n is the index of refraction. Using[9,10] $n = 1.6$ and $\xi_R = 25$ nm gives $\lambda_C^{\text{air}} \approx 500/\kappa$; thus the optical region, which is of primary interest, corresponds to $0.6 < \kappa < 1.4$.

We now justify our use of the weak-field regime to obtain Figs. 1 and 2. We do this by calculating a rigorous lower bound to the field e_N^2 in which the nematic (N) phase becomes thermodynamically stable. It is well known that near this field strength distortions in periodic structures cannot be neglected.[11,12] Our requirement is therefore that e_{th}^2 be significantly smaller than e_N^2. We proceed as follows: (a) The N-phase free-energy minimum is calculated exactly. (b) With use of convenient approximations, the free energies of periodic structures are found in the field region of interest. We consider two cases, that of an undistorted *C* phase and that of an undistorted *Hm* phase. These free energies are necessarily *greater* than the true free energy at any point in the phase diagram. (c) Equating the results of (a) and (b), a field $\bar{e}_N^2$ is obtained which satisfies $\bar{e}_N^2 < e_N^2$.

For (a) we use (9) and, from $\partial f_N/\partial\mu = 0$, obtain

$$\mu^3 = \tfrac{3}{4}\mu^2 + \tfrac{1}{8}t\mu - \tfrac{1}{2}e^2 = 0. \tag{11}$$

Equating $f_{Hm} = f_N$ then determines $\bar{e}_{NHm}^2(t,\kappa)$ with, of course, $\bar{e}_{NHm}^2 < e_N^2$. An analogous procedure yields $\bar{e}_{NC}^2$.

These lower bounds $\bar{e}_{NC}^2$ and $\bar{e}_{NHm}^2$ are shown in Fig. 2. We find that $e_{\text{th}}^2/e_N^2 < 0.27$. In comparison with experimental data,[13-16] this bound justifies our use of the zero-field order-parameter form to calculate the *Hm*-phase threshold field.

All the above results apply equally well to the case of an applied magnetic field **H** with the following re-

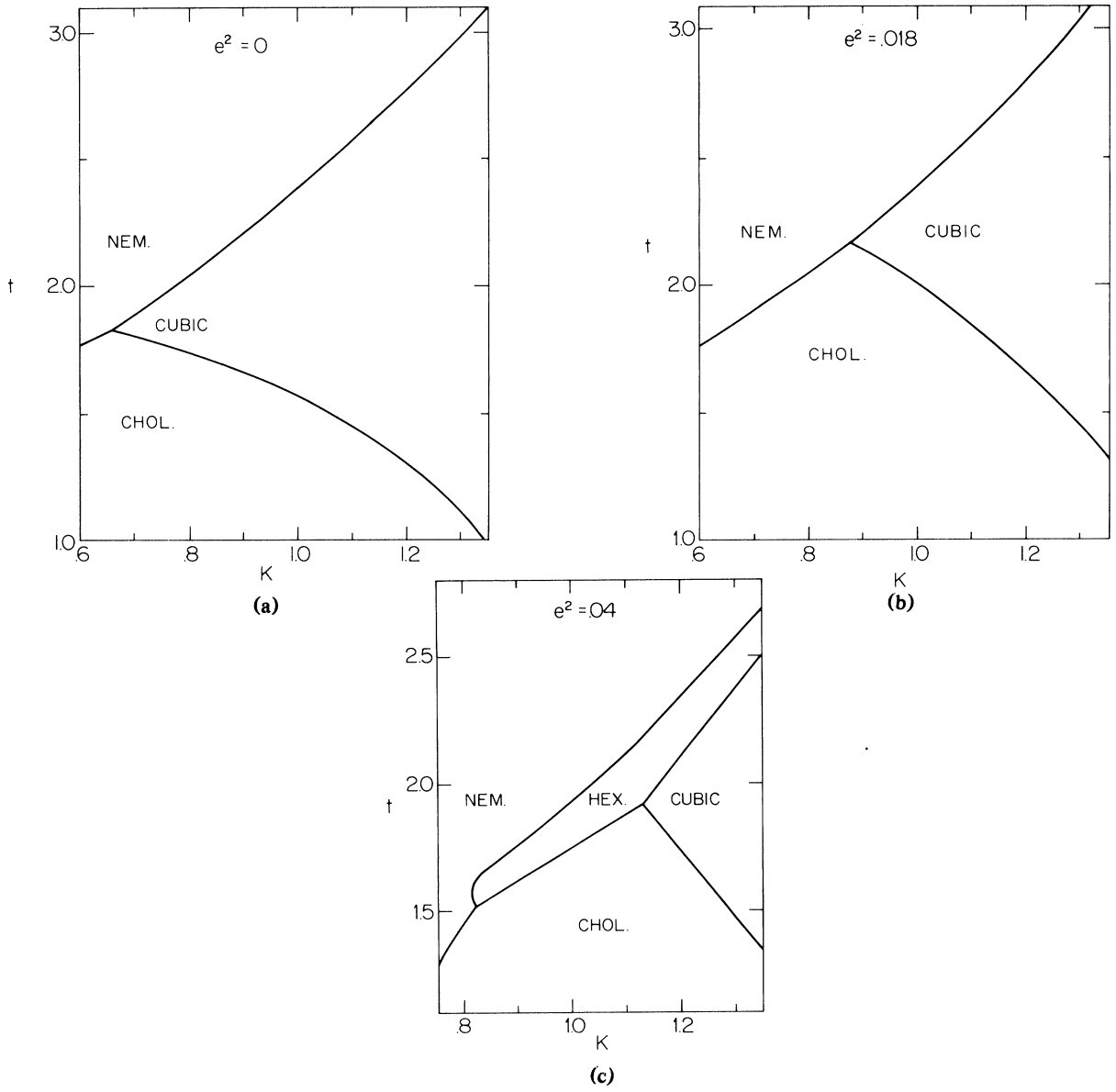

FIG. 1. Thermodynamic phase diagram (chirality-temperature plane) of cholesteric liquid crystals for (a) $e^2=0$, (b) $e^2=0.018$, and (c) $e^2=0.04$.

placements:

$$\chi \leftrightarrow \epsilon,$$

$$(2V)^{-1}H_iH_j\int d^3r\,\chi_{ij} \leftrightarrow (8\pi V)^{-1}E_iE_j\int d^3r\,\epsilon_{ij}, \quad (12)$$

$$(3\gamma^2/\beta^3)^{1/2}H \leftrightarrow (3\gamma^2/4\pi\beta^3)E.$$

[Of course, the phenomenological coefficients appearing in (2) are order-parameter dependent and thus change when a different choice is made.]

Turning to experiment, the relevant quantities are $(\Delta\epsilon)E^2$ and $(\Delta\chi)H^2$. In many cholesteric systems $\Delta\epsilon \simeq 0.1$ but this can vary considerably.[17] On the other hand, $\Delta\chi \simeq 10^{-7}$ in all cases of interest.[17] Noting that the elastic energy density term $\frac{1}{2}c_1\epsilon_{ij,l}^2$ in (2) will appear in the scaled free energy of a uniaxial nematic or racemic mixture as $\frac{3}{4}\xi_R^2\mu^2(n_{i,l})^2$ and that $\mu=\frac{1}{2}$ at the clearing point, we have for the corresponding Frank constant

$$K=(\beta^4/96\gamma^3)\xi_R^2. \quad (13)$$

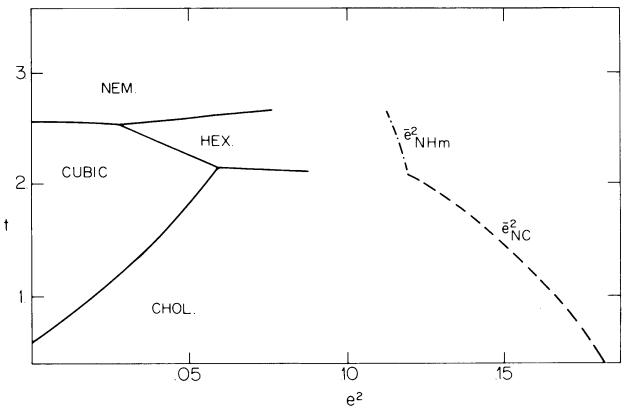

FIG. 2. Thermodynamic phase diagram (applied field-temperature plane) for chirality parameter $\kappa = 1.3$. The boundaries $\bar{e}^2_{NC}$ and $\bar{e}^2_{NHm}$ are lower bounds to the nematic region of the phase diagram.

Using[17] $K = 4\times10^{-7}$ dyn, $\xi_R = 25\times10^{-7}$ cm, $e^2_{th}(\kappa = 1) = 0.018$, and $(\mu_0)_{th} = 0.11$, we obtain

$$(\Delta\epsilon)[E(\text{kv/cm})]^2 = 4.6\times10^3, \qquad (\Delta\chi)[H(\text{Oe})]^2 = 3.6\times10^2. \tag{14}$$

For $\Delta\epsilon = 0.1$ and $\Delta\chi = 10^{-7}$, (14) give $E = 210$ kV/cm and $H = 60$ kOe as the threshold fields for a cholesteric system having a C-phase Bragg back reflection at 500 nm. Such field strengths are experimentally accessible.

Summarizing, we have presented here arguments for the existence of a new 2D hexagonal phase[18] in cholesterics in an applied electric or magnetic field. Verification of this phase's existence and studies of its structure could lead to an improved understanding of the complex behavior exhibited by cholesterics below their clearing point.

We are grateful to H. Grebel for numerical assistance and acknowledge helpful discussions and correspondence with H. Stegemeyer. This work was supported in part by grants from the U.S.–Israel Binational Science Foundation, Jerusalem, Israel, and the Commission for Basic Research of the Israel Academy of Sciences.

[1]For an experimental review, see H. Stegemeyer and K. Bergmann, in *Liquid Crystals of One- and Two-Dimensional Order,* edited by W. Heltrich and G. Heppke (Springer, Berlin, 1980), p. 161. A more recent review is given by P. P. Crooker, Mol. Cryst. Liq. Cryst. **98**, 31 (1983).

[2]S. A. Brazovskii and S. G. Dmitriev, Zh. Eksp. Teor. Fiz. **69**, 979 (1975) [Sov. Phys. JETP **42**, 497 (1976)].

[3]The 2D Bravais lattice is actually triangular; since this structure is generally referred to as hexagonal we do so here also.

[4]R. M. Hornreich and S. Shtrikman, J. Phys. (Paris) **41**, 335 (1980), and **42**, 367(E) (1981).

[5]H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **28**, 1114 (1983). This paper contains extensive references on cholesteric blue phases. We follow the notation in this paper and use *Hm* to distinguish the *modified hexagonal* structure with a $q = 0$ Fourier component in its order parameter from that originally introduced in Ref. 2.

[6]P. G. de Gennes, Mol. Cryst. Liq. Cryst. **12**, 193 (1971).

[7]H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **30**, 3264 (1984).

[8]Note that whereas the $\mathbf{E} = 0$ C-phase order parameter is exact and those for the cubic phases include up to four different wave-vector magnitudes (Refs. 5 and 7), that for the *Hm* phase is restricted to a single nonzero spatial frequency. We shall show elsewhere that the effect of higher harmonics is expected to be small.

[9]D. L. Johnson, J. H. Flack, and P. P. Crooker, Phys. Rev. Lett. **45**, 641 (1980).

[10]C. C. Yang, Phys. Rev. Lett. **28**, 955 (1972).

[11]P. G. de Gennes, Solid State Commun. **6**, 163 (1968).

[12]R. B. Meyer, Appl. Phys. Lett. **14**, 208 (1968).

[13]D. Armitage and R. J. Cox, Mol. Cryst. Liq. Cryst. **64**, 41 (1980).

[14]P. L. Finn and P. Cladis, Mol. Cryst. Liq. Cryst. **84**, 159 (1982).

[15]G. Heppke, M. Kurmrey, and F. Oestreicher, Mol. Cryst. Liq. Cryst. **99**, 99 (1983).

[16]F. Porsch and H. Stegemeyer, Phys. Rev. A **30**, 3369 (1984).

[17]See, e.g., P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974), or M. J. Stephen and J. P. Stanley, Rev. Mod. Phys. **46**, 617 (1974).

[18]The hexagonal phase can be envisaged as an assembly of parallel infinite cylinders whose axes pass through the sites of a planar triangular lattice. The equilibrium order-parameter configuration for a *single* such cylinder is given by R. M. Hornreich, M. Kugler, and S. Shtrikman, Phys. Rev. Lett. **48**, 1404 (1982). Such cylinders can also be interlaced to form the cubic BP, as shown in Figs. 5 and 6 in Ref. 7.