Icosahedral ordering in cholesteric liquid crystals

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The blue phases of cholesteric liquid crystals are analyzed in the Landau theory. A region in which a phase with icosahedral symmetry has the lowest energy is found on the phase diagram. The relative intensities of the Bragg reflections are calculated for the scattering of light by an icosahedral structure. The fog phase observed experimentally may correspond to an icosahedral ordering.

The nature of the blue phases of cholesteric liquid crystals, BPI and BPII, has been under study for several years now.[1–3] An expansion of the free energy of the system, F, in powers of the order parameter $Q_{\alpha\beta}(\mathbf{r})$ (the traceless part of the dielectric tensor of the medium),

$$F - F_0 = (1/2)\int d\mathbf{r}[a_0(T-T^*)(Q_{\alpha\beta})^2 + b(\partial_\alpha Q_{\beta\gamma})^2 + c(\partial_\alpha Q_{\alpha\gamma})^2 + 2bq_0 e_{\alpha\beta\gamma}Q_{\alpha\mu}\partial_\beta Q_{\gamma\mu}]$$

$$+ \int d\mathbf{r}[\mu Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \lambda(Q_{\alpha\beta}Q_{\gamma\delta})^2], \qquad (1)$$

leads to the appearance on the phase diagram (the diagram of the temperature T and the chirality parameter q_0) of regions in which phases with a three-dimensional periodicity of the tensor $Q_{\alpha\beta}(\mathbf{r})$ exist. The phase BPI has an O^8 bcc structure, while BPII has an O^2 simple cubic structure.[2,3] The nature of the blue fog phase, BPIII, is not yet clear. The observation of a blurred step in the optical transmission spectrum[4] $R(\lambda)$ in BPIII and, correspondingly, of a broad peak in the optical scattering spectrum[5] $I(\lambda)$ is linked with a short-range order at the correlation length $\xi \sim 5a$, where $a = I/q_0 \sim 300$ Å. A special treatment of the plates bounding the sample leads to a strong orienting effect for BI and BPII: The initial size of the domains, $L \sim 30a$, of polycrystalline BPI and BPII samples increases by an order of magnitude. Under the same conditions, the spectra $R(\lambda)$ and $I(\lambda)$ for BPIII do not change.

In the present study we show that, under certain conditions the free energy of a phase with icosahedral symmetry is lower than the free energies of the BPI and BPII phases, and we offer the hypothesis that the phase BPIII corresponds to an icosahedral ordering. We calculate the relative intensities of the Bragg reflections for the scattering of light by an icosahedral structure.

Working from the Landau theory for a single harmonic of the order parameter (the wave vectors $\mathbf{q}_j^2$, along the edges of the icosahedron), Kleinert and Maki[6] found that the temperature (T_{ic}) of the first-order phase transition from the isotropic phase to the icosahedral phase is significantly lower than the temperature (T_c) of the transition from the isotropic phase to non-one-dimensional structures (a hexagonal structure and the O^5 bcc structure): $(T_{ic} - T^{**}) < 0.2(T_c - T^{**})$, where $T^{**} = T^* - bq_0^2/a_0$ is the temperature of the absolute instability of the isotropic phase. We can show that incorporating the higher harmonics, which are used in the study of the cubic BPI and BPII phases,[2] changes the situation in a qualitative way.

Let us consider the harmonics of an icosahedral structure with the wave vectors $\mathbf{q}_j^n$, whose magnitude $q(n)$ lies in the range of the wave vectors of the fundamental harmonics of BPI and BPII: $q(n) = 0.951$, 1.0, 0.535, 0.618, 1.176, 1.380, 1.414, 1.618, 1.704, 1.732, 1.877, 1.902, 1.902, and 2.0 ($n = 1,...,14$, respectively)[1)] and $p(n) = 1,\sqrt{2},\sqrt{3},2$ for BPI and BPII. We write the order parameter in the form

$$Q_{\alpha\beta}(\mathbf{r}) = \sum_n \sum_i \epsilon(n) \{ l_\alpha(\mathbf{q}_i^n) l_\beta(\mathbf{q}_i^n) \exp(i\mathbf{q}_i^n \mathbf{r} + \varphi_i(n)) + \text{c.c.} \} / \sqrt{M(n)}, \tag{2}$$

where $M(n)$ is the number of wave vectors $\mathbf{q}_i^n$ of the harmonic n [$M(1) = M(13) = 12$, $M(3) = 20$, $M(2) = M(4) = M(8) = M(14) = 30$, and otherwise $M(n) = 60$], $l_\alpha(\mathbf{q}) = [m_\alpha(\mathbf{q}) + im'_\alpha(\mathbf{q})]/\sqrt{2}$, and the real vectors $\mathbf{m}(\mathbf{q})$, $\mathbf{m}'(\mathbf{q})$, $\mathbf{q}/q$ form a right-handed triad of unit vectors. Here $l_\alpha(\mathbf{q}) l_\beta(\mathbf{q})$ one of the five eigenmodes of the tensor $Q_{\alpha\beta}(q)$, corresponds to the lowest eigenvalue of the quadratic part of expression (1). Working from (1) and order parameter (2), which contains $N = \Sigma M(n)/2$ phases, we find an expression for F which contains $N-6$ independent combinations ψ_j of these phases. The six remaining independent combinations of phases, which are not affected by the minimization of F, correspond to six Goldstone modes, three of which are ordinary "acoustic" excitations of the order parameter $Q_{\alpha\beta}(\mathbf{r})$, while the three others are "phasons."[7,8] After finding those combinations of phases which correspond to the completely symmetric representation of the icosahedral group, and after a minimization of expression (1) with respect to $\epsilon(n)$, we find the following relations: $\epsilon(2)/\epsilon(1) \approx 0.5$, $\epsilon(8)/\epsilon(1) \simeq 0.2$, $\epsilon(n)/\epsilon(1) \lesssim 0.05$ for the other $n (k = q_0\sqrt{12\lambda b}/\beta \gtrsim 1.5)$. Here is a dimensionless expression for F which includes only the three fundamental harmonics:

$$\begin{aligned}(F - F_0)(36\lambda^3/\mu^4) = {} & \Sigma\, (t - k^2 + k^2(rq(n)/q(1) - 1)^2)\mu_n^2/4 - 2.8249\,\mu_1^2\mu_2 \\ & - 1.5875\,\mu_1^2\mu_8 + 0.4496\,\mu_2^3 - 0.2031\,\mu_2^2\mu_8 + 1.8455\,\mu_2\mu_8^2 + 0.0075\mu_8^3 \\ & + 1.2333\mu_1^4 + 3.9728\,\mu_1^2\mu_2^2 + 1.4996\,\mu_1^2\mu_2\mu_8 + 2.3652\,\mu_1^2\mu_8^2 + 1.3536\,\mu_2^4 \\ & + 0.4755\,\mu_2^3\mu_8 + 2.4346\,\mu_2^2\mu_8^2 - 0.2176\mu_2\mu_8^3 + 1.1504\mu_8^4\,,\end{aligned} \tag{3}$$

where $\mu_n = \sqrt{6}\lambda\epsilon(n)/\mu, t = 12\lambda a_0(T - T^*)/\mu^2$, $r = [\Sigma\mu_n^2 q(n)/q(1)]/[\Sigma\mu_n^2 q^2(n)/q^2(1)]$ and the sum includes $n = 1$, 2, 8. A minimization of expression (3) leads to a phase diagram (Fig. 1) in which we consider as competing phases the phase with icosahedral symmetry and the phases observed experimentally: the isotropic phase, BPI, BPII, and the cholesteric phase. In the BPII region, the dashed line is the line of the transition between the isotropic and icosahedral phases. In the minimization of F for BPI and BPII, we take the first four harmonics into account (with the wave vectors [110], [200], [211], [220] and [100], [110], [111], [200], respectively).[2]

How do the experimental data on the fog phase compare with the properties of an icosahedral phase? In the case of nonorienting boundaries, the fog phase is in a polycrystalline state, as BPI and BPII are. A possible explanation of the larger size of the domains in BPI and BPII is that the cubic structures are more anisotropic than the completely symmetric icosahedral structure (crudely speaking, an icosahedron is closer than a cube to being a sphere). The effect of the additional "phason" degrees of freedom on the size of the domains can be understood by analyzing the orienting effect of the boundaries on liquid-crystal samples in a blue phase. For BPI and BPII, the effect of the boundaries reduces to one of orienting one of the vectors of the fundamental harmonic ([110] or [100]) in the direction perpendicular to the boundary plane.[9] The general ("acoustic") phase of the order parameter is then fixed, and the domain undergoes a regular growth. When phasons are present, an orientational pinning of the phase of one of the harmonics does not fix the order parameter in a domain. The phason degrees of freedom of the "quasicrystal" determine the formation and growth of polycrystalline regions in a manner not controlled by the boundary. The situation corresponds to an independence of the $I(\lambda)$ and $R(\lambda)$ spectra in BPII from the treatment of the boundary surfaces.[4,5] In order to bring out the phason mechanism for the formation of polycrystalline regions, it would be desirable to measure the spectra $I(\lambda)$ and $R(\lambda)$ in cyanobiphenyl cholesteric liquid crystals, which exhibit a relatively larger dielectric anisotropy, $\Delta\epsilon \simeq 1$, with the goal of intensifying orientation processes.

The phase diagram (Fig. 1) is in qualitative agreement with the experimental observation of BPII in short-pitch ($k \gtrsim 2.5$) cholesteric liquid crystals. The values of F for BPI, BPII, and the icosahedral phase are exceedingly close together [at $K \geqslant 1$, $(T_c - T_{ic})/(T_c - T^{**}) \leqslant 0.1$, where T_c is the temperature of the transition between the isotropic phase and BPII]. For this reason, the shift of the region of the icosahedral phase to slightly larger values of the parameter, $k \geqslant 2.5$, which we found (the values corresponding to standard short-pitch cholesteric liquid crystals are $k \simeq 1.5$–2), may therefore be a consequence of going beyond the accuracy of the calculation of F according to the Landau expansion in (1) or the higher harmonics, with $q(n)/q(2) > 2$, which we have not considered here. More-reliable results of the Landau expansion are the relations between $\epsilon(n)$, which can be used for an experimental identification of the icosahedral phase. The wave vectors of the first two harmonics are too close in magnitude $[q(2) - q(1) \simeq 0.05q(2)]$ to allow the corresponding peaks, $I_1(\lambda)$ and $I_2(\lambda)$, to be distinguished from the broad peak $I(\lambda)$ which is observed in

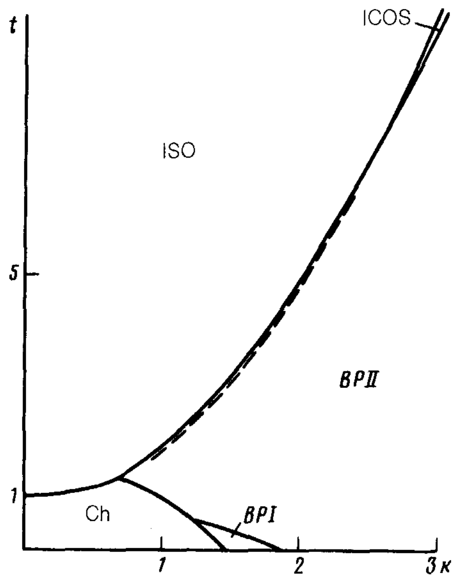

FIG. 1.

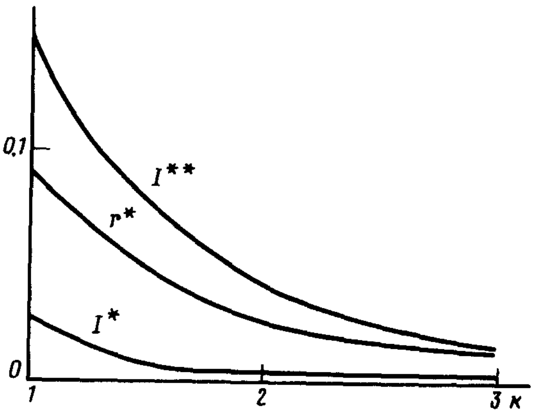

FIG. 2.

BPIII (with a half-width $\Delta\lambda\simeq 0.2\lambda_0$) Consequently, the identification of the icosahedral phase may come from the observation of $I_n(\lambda)$ or $R_n(\lambda)$ steps corresponding to harmonics with $n>2$. Figure 2 shows the relative heights of the peaks corresponding to the wavelengths $\lambda^*\simeq\lambda_0/\sqrt{2}$ and $\lambda^{**}\simeq\lambda_0/\sqrt{3}$ (I^* and I^{**}, respectively). Also shown here is the behavior of the relative shift r^* (the "red shift") of the broad main peak with respect to the position of the peak in $I(\lambda)$ for the cholesteric phase. In order of magnitude, the values of r^* correspond to the experimental results which have been published.[10] The values of I^* (at $k\leqslant 1.5$) and of I^{**} (at $k\leqslant 3$) lie within the accuracy attainable in the measurements of $I(\lambda)$. The absence of a peak in $I(\lambda)$ at $\lambda_0/\sqrt{2}$, mentioned in Ref. 5, is apparently due to either an inadequate measurement accuracy or a relatively large value of the parameter k for this cholesteric liquid crystal.

After this study was completed, I learned of the contents of a preprint by Hornreich and Shtrikman, who derived an expression for the free-energy functional in (1) including the harmonics $\epsilon(1)$ and $\epsilon(2)$. They also suggested that the higher harmonics might make an icosahedral phase favorable from the energy standpoint and that this icosahedral phase might correspond to the fog phase.

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[1)] $q(12)=q(13)$, but $\mathbf{q}_i^{12}\neq\mathbf{q}_j^{13}$ for arbitrary $1\leqslant i\leqslant M(12)$ and $1\leqslant j\leqslant M(13)$.

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