Bond Orientational Order in the Blue Phases of Chiral Liquid Crystals

Lech Longa* and Hans-Rainer Trebin
Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany
(Received 17 May 1993)

It is proposed to describe blue phases by two order parameters: the standard alignment tensor field $Q_{\alpha\beta}(\boldsymbol{r})$ and a bond orientational tensor order parameter of octahedral point group symmetry $\mathcal{O}(\mathbf{432})$. The yet mysterious blue fog then emerges as a liquid of purely cubic bond orientational order. In the transition from the cubic blue phases to the blue fog the cubic space group symmetry is being reduced to its octahedral factor group. Because of the new order parameter the $\mathcal{O}^5(\mathcal{I}432)$ structure, which in all previous calculations proved most stable, but never has been detected in experiment, is eliminated from the phase diagram.

PACS numbers: 64.70.Md, 05.70.Ce, 61.30.–v, 61.50.Em

Chirality is an important issue in liquid crystal physics. It leads to fundamentally new phases like the layered smectic-C^* phases, the smectic-A^* "Abrikosov" phase, and the blue phases. Some compounds exhibit up to three distinct blue phases labeled BPI, BPII, and BPIII with ascending temperature [1,2]. BPIII is commonly referred to as blue fog. It is widely accepted that the blue phases are liquids, where the long molecular axes form orientational patterns periodic in three directions of space, and that BPI carries a body-centered cubic structure of space group symmetry $\mathcal{O}^8(\mathcal{I}4_132)$, BPII a simple cubic structure of space group symmetry $\mathcal{O}^2(\mathcal{P}4_232)$ [1,2]. The structure of the blue fog, however, which is formed directly on cooling the isotropic liquid, has yet defied satisfactory explanation. Contrary to BPI and BPII, the blue fog does not exhibit Bragg scattering of light but, instead, shows a broad reflection band typical for an amorphous system [1,3,4].

Several models have been proposed for the blue fog structure: (a) *an amorphous model* [1] where BPIII is viewed as a second isotropic liquid, but with a different local structure; (b) *an icosahedral model* [1,5,6] where BPIII is assumed to possess a quasiperiodic icosahedral symmetry, similar to that of the binary metallic quasicrystals; and (c) *a model of bond orientational order* [7].

Only the icosahedral model has been accessible to analytical and numerical calculations of the free energy and of the corresponding phase diagrams. But the results show [6] that none of the many tested quasiperiodic icosahedral structures is stable just below the isotropic liquid. Instead, theory with great certainty predicts a body-centered cubic structure of space group $\mathcal{O}^5(\mathcal{I}432)$ on that part of the phase diagram where BPIII is seen [8]. But an $\mathcal{O}^5$ structure has never been detected experimentally in chiral liquid crystals.

Thus it seems that there are two probably correlated problems for a correct theory: first a credible model for the structure of the blue fog and, second, a mechanism that destabilizes the $\mathcal{O}^5$ structure.

In this Letter we argue that the solution to both problems is fluctuations of the orientational order, destroying the BPI and BPII lattices. One model emerging for the blue fog is that although the translational order of BPI or BPII is being lost due to the fluctuations, a cubic orientational order remains. Such a concept was long ago envisaged by Nelson and Toner [9]. The phenomenon where due to large displacive fluctuations of the atomic positions or due to the unbinding of dislocation dipoles the translational order is destroyed, but the bonds of the different atomic clusters remain oriented, is denoted "bond orientational order." In blue phases one has to imagine that the periodic sequence of cubic unit cells or—as frequently depicted—of disclination lines, is interrupted, but that substructures of the cells or parts of the disclination array preserve a cubic alignment. Despite the fact that in this sense there are no bonds in the blue phases, we continue to use the notion "bond orientational order."

The order of the molecular axes is described by a traceless and symmetric quadrupole tensor field $\boldsymbol{Q}(\boldsymbol{r})$ which we divide into a mean field part $\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r})$ of periodic (or quasiperiodic) symmetry $\mathcal{G}$ and a contribution $\boldsymbol{Q}^{\delta}(\boldsymbol{r})$ from fluctuations: $\boldsymbol{Q}(\boldsymbol{r}) = \boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r}) + \boldsymbol{Q}^{\delta}(\boldsymbol{r})$. We express the bond orientational order by a hexadecupole moment in the form of a fourth rank tensor $B_{\alpha\beta\mu\nu}$. Its corresponding observable is a nonlinear dielectric susceptibility $\bar{\varepsilon}_{\alpha\beta\mu\nu}$, which actually has been detected in cubic blue phases by Pierański *et al.* [10]. The main result of our calculations is that in a large range of the phenomenological parameters a pure bond oriented phase [$\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r}) \equiv 0$, $B_{\alpha\beta\mu\nu} \neq 0$] becomes stable in the temperature-chirality regime of the blue fog. Cubic phases of $\mathcal{O}^2$ and $\mathcal{O}^8$ structure with finite values of both order parameters appear in the neighborhood. The free energy of phases, whose quadrupole-tensor field lacks wave vectors in reciprocal space along the simple cubic axes of $[n00]$-type ($n = 1, 2, ...$), is enhanced by coupling terms of both order parameters. *This is the case for the $\mathcal{O}^5$ structure, and it is the mechanism by which the $\mathcal{O}^5$ structure is destabilized.*

To start we establish a general de Gennes–Wilson-Ginzburg-Landau free energy as a functional integral:

$$F[\boldsymbol{Q}(\boldsymbol{r})] = \mathcal{F}_{deGL}[\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r})] - \kappa^2\bar{\beta}^{-1}\ln\int \mathcal{D}\boldsymbol{Q}^{\delta}(\boldsymbol{r})\exp(-\bar{\beta}\kappa^{-2}\{\mathcal{F}_{deGL}[\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r}) + \boldsymbol{Q}^{\delta}(\boldsymbol{r})] - \mathcal{F}_{deGL}[\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r})]\}) \,. \quad (1)$$

The standard mean field free energy $\mathcal{F}_{deGL}$ divides into

$$\mathcal{F}_{deGL}[\boldsymbol{Q}(\boldsymbol{r})] = v^{-1}\int d^3\boldsymbol{x}\{\,\mathcal{F}_{elastic}[\boldsymbol{Q}(\boldsymbol{r}), \partial\boldsymbol{Q}(\boldsymbol{r})] + \mathcal{F}_{bulk}[\boldsymbol{Q}(\boldsymbol{r})]\}\,, \quad (2)$$

where in terms of dimensionless units introduced by Grebel *et al.* [8] the elastic and the bulk parts read

$$\mathcal{F}_{elastic}[\boldsymbol{Q}(\boldsymbol{r}), \partial\boldsymbol{Q}(\boldsymbol{r})] = \frac{1}{4}\kappa^2\{[\,\epsilon_{imn}Q_{nj,m} - Q_{ij}]^2 + \rho[Q_{ij,j}]^2\}, \quad (3)$$

$$\mathcal{F}_{bulk}[\boldsymbol{Q}(\boldsymbol{r})] = \tau\,\mathrm{tr}\boldsymbol{Q}^2 - \sqrt{6}\,\mathrm{tr}\boldsymbol{Q}^3 + (\mathrm{tr}\boldsymbol{Q}^2)^2. \quad (4)$$

κ is the chirality parameter, t the standard reduced temperature of Landau theory, $\tau = \frac{1}{4}(t-\kappa^2)$ the renormalized reduced temperature entering naturally as a parameter in the high-chirality limit, ρ an elastic constant, T the absolute temperature, and $\bar{\beta} = (k_BT)^{-1}\kappa^2$.

The most probable mean-field configuration $\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r})$ is a "saddle point" of the functional integral (1). It is obtained in practice by a plane wave ansatz for all relevant periodic and quasiperiodic tensor fields,

$$\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r}) = \sum_{{}^*\boldsymbol{k}} \frac{1}{\sqrt{N_{{}^*\boldsymbol{k}}}}\left\{\sum_{\boldsymbol{k}\in{}^*\boldsymbol{k}}\left[\sum_{m=-2}^{2} Q_m(\boldsymbol{k},\boldsymbol{r})\right]\boldsymbol{e}^{[2]}_{m,\hat{\boldsymbol{k}}}\right\}, \quad (5)$$

where

$$Q_m(\boldsymbol{k},\boldsymbol{r}) = Q_m(|\boldsymbol{k}|)\cdot\exp(i\,\boldsymbol{k}\cdot\boldsymbol{r} - i\psi_{m,\hat{\boldsymbol{k}}}). \quad (6)$$

The wave vectors $\boldsymbol{k}$ are taken out of the reciprocal lattice of a space group $\mathcal{G}$, where ${}^*\boldsymbol{k} = \{\boldsymbol{k}' : \boldsymbol{k}' = S\boldsymbol{k}, \{S|\boldsymbol{t}\}\in\mathcal{G}\}$ is the star of $\boldsymbol{k}$; $\mathbf{N}_{{}^*\boldsymbol{k}}$ is the number of prongs of the star ${}^*\boldsymbol{k}$, $Q_m(|\boldsymbol{k}|)$ are the variational parameters in the expansion, and finally $\boldsymbol{e}^{[2]}_{m,\hat{\boldsymbol{k}}}$ are the spin $L=2$ tensors represented in an orthogonal, right-handed local coordinate system with $\hat{\boldsymbol{k}}$ as quantization axis (for a precise definition see [8,11]). We are going to replace the second term of Eq. (1), describing the influence of the fluctuations, by an effective functional containing the bond order parameter. But first let us motivate this practice by an analysis of the high-chirality limit [1,5] of the free energy (1), which is established for $\kappa\to\infty$ with $\tau = \text{const}$, $\bar{\beta} = (k_BT)^{-1}\kappa^2 = \text{const}$, and $F/\kappa^2 = \text{const}$. The bulk part of $\mathcal{F}_{deGL}/\kappa^2$ then vanishes, and the ground state is determined exclusively by the elastic part.

In Refs. [1,5] it is demonstrated that the ground state of (2) for the high chirality limit, denoted $\boldsymbol{Q}^{hcl}(\boldsymbol{r})$, consists of an arbitrary linear combination of the plane wave tensor modes with helicity $m=2$ and wave vectors of the sphere $|\boldsymbol{k}|=1$. This ground state is continuously degenerate and has the same free energy as the isotropic liquid state. For finite chiralities the degeneracy of $\boldsymbol{Q}^{hcl}$ is removed by the bulk free energy. The most stable structure just below the isotropic liquid found to date has $\mathcal{O}^5$ symmetry.

Thermal fluctuations, not taken into account in this mean-field analysis, may change the scenario drastically. Let us fix τ and $\bar{\beta}$ in the free energy expression (1) and increase κ. The free energy difference, $\kappa^{-2}(\Delta F)$ between ground states of various space group structures with $m=2$ and wave vectors selected from the sphere $|\boldsymbol{k}|=1$ vanishes, and the energy of the infinite chirality state is of order κ^{-2}. Thus, for κ large enough, fluctuations lead from one state to another and destroy any space group structure, including $\mathcal{O}^5$.

Some implications of the fluctuation processes as described above have been analyzed by Brazovskii *et al.* [12]. Here we will follow a line of thought where the fluctuations are assumed to mix different cubic space group symmetries. Thus they destroy their translational symmetry, but preserve what is common, namely, the factor group symmetry elements. Generalizing the results of Nelson and Toner [9] and of Jarič [13] we introduce a (spatially constant) bond orientational tensor order parameter $B_{\alpha\beta\mu\nu}$. It can be divided into irreducible tensors $B^L_{\alpha\beta\mu\nu}$ of the rotation group SO(3) with momenta $L=0$, 2, and 4. We aim at a hexadecupolar order parameter, and hence only take regard of the $L=4$ part $B^4_{\alpha\beta\mu\nu}$. The corresponding nonlinear dielectric susceptibility $\bar{\varepsilon}^4_{\alpha\beta\mu\nu}$ is responsible for an alignment of BPI and BPII crystallites and has been studied in experiments of Pierański *et al.* [10].

The fluctuation part of the free energy (1) is now replaced by an effective SO(3)-invariant polynomial $\mathcal{F}_{coupl}[\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r}), \boldsymbol{B}^4]$, coupling the alignment tensor field $\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r})$ to $\boldsymbol{B}^4$, and a polynomial $\mathcal{F}_{bond}[\boldsymbol{B}^4]$ solely in the components of $\boldsymbol{B}^4$:

$$F[\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r}), \boldsymbol{B}^4] = \mathcal{F}_{deGL}[\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r})] + \mathcal{F}_{coupl}[\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r}), \boldsymbol{B}^4] + \mathcal{F}_{bond}[\boldsymbol{B}^4]. \quad (7)$$

The lowest-order coupling terms involve one coupling constant λ:

$$\mathcal{F}_{coupl}[\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r}), \boldsymbol{B}^4] = -\frac{\lambda}{3}B^4_{\alpha\beta\gamma\delta}\int d^3\boldsymbol{r}[Q^{\mathcal{G}}_{\alpha\beta}(\boldsymbol{r})Q^{\mathcal{G}}_{\gamma\delta}(\boldsymbol{r}) + Q^{\mathcal{G}}_{\alpha\gamma}(\boldsymbol{r})Q^{\mathcal{G}}_{\beta\delta}(\boldsymbol{r}) + Q^{\mathcal{G}}_{\alpha\delta}(\boldsymbol{r})Q^{\mathcal{G}}_{\gamma\beta}(\boldsymbol{r})]. \quad (8)$$

For a positive definite free energy $\mathcal{F}_{bond}$ must be expanded up to fourth order in $\boldsymbol{B}^4$ and contains four independent coefficients [13]:

$$\mathcal{F}_{bond}[\boldsymbol{B}^4] = a_2B^4_{\alpha\beta\gamma\delta}B^4_{\alpha\beta\gamma\delta} + a_3B^4_{\alpha\beta\gamma\delta}B^4_{\alpha\beta\mu\nu}B^4_{\gamma\delta\mu\nu} + a_{4,1}(B^4_{\alpha\beta\gamma\delta}B^4_{\alpha\beta\gamma\delta})^2 + a_{4,2}B^4_{\alpha\beta\gamma\delta}B^4_{\gamma\delta\mu\nu}B^4_{\mu\nu\rho\sigma}B^4_{\rho\sigma\alpha\beta}\,, \quad (9)$$

where according to Landau the weight of the quadratic part depends on the thermostatic control parameters: $a_2 = a_2(\tau, \kappa^2)$.

As a global minimization of the functional (7) is extremely difficult, we follow a standard procedure to minimize the $\mathcal{F}_{bond}[\boldsymbol{B}^4]$ part first. The "bond orientation" phase diagram for the free energy (9) over the space of phenomenological coefficients a_2, a_3, $a_{4,1}$, $a_{4,2}$ has been analyzed in detail by Jarič [13]. There are only three point groups allowed for tensors minimizing (9) adjacent to the isotropic state: O_h, $D_{\infty h}$, and D_{4h}. The phase diagram is dominated by the octahedral structure O_h, which is accessed through either a first-order phase transition or a multicritical continuous transition [13]. The transition isotropic to $D_{\infty h}$ is only of first order, whereas the transition isotropic to D_{4h} is only of second order and the least probable one, as it requires $a_2 = a_3 = 0$. Therefore, and because structures of $D_{\infty h}$ symmetry have not been detected experimentally in the blue phases, we restrict ourselves to the space of O_h-symmetric hexadecupole tensors, which reads

$$B^4_{\alpha\beta\gamma\delta} = B_0 \tilde{B}_{\alpha\beta\gamma\delta} = B_0 \sqrt{2}\sqrt{5}\sqrt{7} \times \{\sqrt{\tfrac{5}{14}}[(\boldsymbol{e}^{[4]}_{4,\hat{\boldsymbol{u}}}) + (\boldsymbol{e}^{[4]}_{-4,\hat{\boldsymbol{u}}})] + (\boldsymbol{e}^{[4]}_{0,\hat{\boldsymbol{u}}})\}_{\alpha\beta\gamma\delta}. \quad (10)$$

Here B_0 is the norm of $\boldsymbol{B}$, and $\boldsymbol{e}^{[4]}_{m,\hat{\boldsymbol{u}}}$ are the spin $L = 4$ tensors represented in an orthogonal, right-handed basis tripod $\{\hat{\boldsymbol{u}}_1, \hat{\boldsymbol{u}}_2, \hat{\boldsymbol{u}}_3 \equiv \hat{\boldsymbol{u}}\}$ with $\hat{\boldsymbol{u}}$ as quantization axis.

The free energy (9) over the space of cubic tensors (10) only depends on B_0:

$$\mathcal{F}_{bond}[\boldsymbol{B}^4] = a(\kappa^2, \tau) B_0^2 - b B_0^3 + c B_0^4, \quad (11)$$

where b and $c > 0$ are combinations of the coefficients a_i (9) and as such arbitrary. From the observations of Pierański *et al.* [10] it follows that the quartic form $\hat{n}_\alpha \hat{n}_\beta \hat{n}_\gamma \hat{n}_\delta \, B^4_{\alpha\beta\gamma\delta}$ has maxima along the faces of the cube (the tensor is "pronged" rather than "pierced," similarly as uniaxial quadrupole tensors may be prolate and oblate). Therefore $B_0 > 0$, and the parameter b must be positive. Scaling B_0 appropriately, we can set $b = 1$.

For arbitrary control parameters (κ,τ) and for fixed values of the remaining coefficients, the minimization is now performed along the following route: The free energy at this stage depends on $\boldsymbol{Q}^{\mathcal{G}}$, the norm B_0 of $\boldsymbol{B}^4$ and the orientation of $\boldsymbol{B}^4$ with respect to the laboratory frame, expressed by the tripod $\{\hat{\boldsymbol{u}}_1, \hat{\boldsymbol{u}}_2, \hat{\boldsymbol{u}}\}$. $\boldsymbol{Q}^{\mathcal{G}}(\boldsymbol{r})$ is as usual expanded into plane waves with helicity as in Eq. (5). For practical calculations we restrict this expansion to two leading stars ($^*\boldsymbol{k}_1$,$^*\boldsymbol{k}_2$) in reciprocal space and select only $m = 2$ modes, which correspond to the low-lying branch of the excitation spectrum for the quadratic part of $\mathcal{F}_{deGL}$ [8]. Hence the minimization procedure is reduced to a minimization over the space of amplitudes $Q_m(|\boldsymbol{k}|)$. The orientation of the tripod is determined by minimization of the coupling term (8), which now reads

$$\mathcal{F}_{coupl} = -\frac{\lambda}{3} B \sum_{^*k \in \mathcal{G}} \frac{1}{N_{^*k}} [Q_2(|\boldsymbol{k}|)]^2 \tilde{B}_{\alpha\beta\gamma\delta}(\{\hat{\boldsymbol{u}}_1, \hat{\boldsymbol{u}}_2, \hat{\boldsymbol{u}}\}) \times \tilde{E}_{[\alpha\beta\gamma\delta]}(^*\boldsymbol{k}), \quad (12)$$

where

$$\tilde{E}_{[\alpha\beta\gamma\delta]}(^*\boldsymbol{k}) = \sum_{\boldsymbol{k} \in {}^*\boldsymbol{k}} (\boldsymbol{e}^{[2]}_{2,\hat{\boldsymbol{k}}})_{[\alpha\beta} (\boldsymbol{e}^{[2]}_{-2,\hat{\boldsymbol{k}}})_{\gamma\delta]} \quad (13)$$

is the fourth rank tensor. For all the cubic space groups it has octahedral symmetry O_h with the fourfold symmetry axes parallel to the laboratory frame. $[\alpha\beta\gamma\delta]$ denotes symmetrization over all indices.

The orientation of the tripod $\{\hat{\boldsymbol{u}}_1, \hat{\boldsymbol{u}}_2, \hat{\boldsymbol{u}}\}$, minimizing (12), is found with the help of standard quaternion parametrization, and for $\lambda > 0$ can be summarized as follows: (a) If $^*\boldsymbol{k} = [n, 0, 0]$, $-\tilde{B}_{\alpha\beta\gamma\delta}(\{\hat{\boldsymbol{u}}_1, \hat{\boldsymbol{u}}_2, \hat{\boldsymbol{u}}\}) \times \tilde{E}_{[\alpha\beta\gamma\delta]}(^*\boldsymbol{k}) \equiv -\tilde{\boldsymbol{B}}\ \tilde{\boldsymbol{E}}$ is minimal for a tripod constructed out of [100] directions, and maximal for a tripod constructed out of [122] directions. (b) If $^*\boldsymbol{k} = [n, n, 0]$ or $[n, n, 2n]$ it is just the opposite. Now the phase diagrams can be analyzed numerically, assuming that $a(\kappa^2, \tau)$ of Eq. (11) is linear in τ and κ^2: $a(\kappa^2, \tau) = \tilde{a}(\tau - \tilde{b}\kappa^2) - \tilde{\tau}$, where $\tilde{a}$, $\tilde{b}$, and $\tilde{\tau}$ are parameters. As an example we studied phase diagrams in the region $\tilde{a} \approx 1$, $\tilde{b} \approx 1$, $\tilde{\tau} \approx 0$.

For $\lambda < 0$ the phase diagrams are similar to those of the standard theory of blue phases [8]. Cases with bond oriented phase and $\mathcal{O}^5$ structure on the same phase diagram are also found. For $\lambda > 0$, however, the coupling term (12) enhances the equilibrium values of the $Q_2([n00])$ amplitudes which lowers the free energy of $\mathcal{O}^2$ and $\mathcal{O}^8$ and, consequently, *the $\mathcal{O}^5$ structure is destabilized.* The bond oriented phase may appear directly below the isotropic phase. To illustrate this behavior a typical phase diagram is presented in Fig. 1(a). All phase transitions involved are first order.

For the parameter range of Fig. 1(a) we did not find the $\mathcal{O}^8$ phase to be absolutely stable. This feature is characteristic of all two-star calculations [8]. Our analysis, however, clearly shows that due to the presence of bond order the stability of the $\mathcal{O}^8$ is considerably enhanced over the $\mathcal{O}^5$. This is demonstrated in Fig. 1(b), for which $\mathcal{O}^2$ has not been included.

The present analysis, solely restricted to cubic space groups, makes no definite statement about the stability of the cholesteric phase, where $B_0 = 0$. As the coupling term (12) vanishes in this case there is no extra gain in the free energy due to the bond order. Consequently, for all phase diagrams similar to Fig. 1(a), the cholesteric phase is always less stable than the bond oriented phase and at least the high temperature part of the $\mathcal{O}^2$. Details depend upon an arbitrary energy scale of the bond free energy (11) which has been ruled out in our analysis.

Summarizing, the theory of blue phases should include, in addition to the standard quadrupolar alignment tensor field $\boldsymbol{Q}$, an order parameter for the cubic bond-

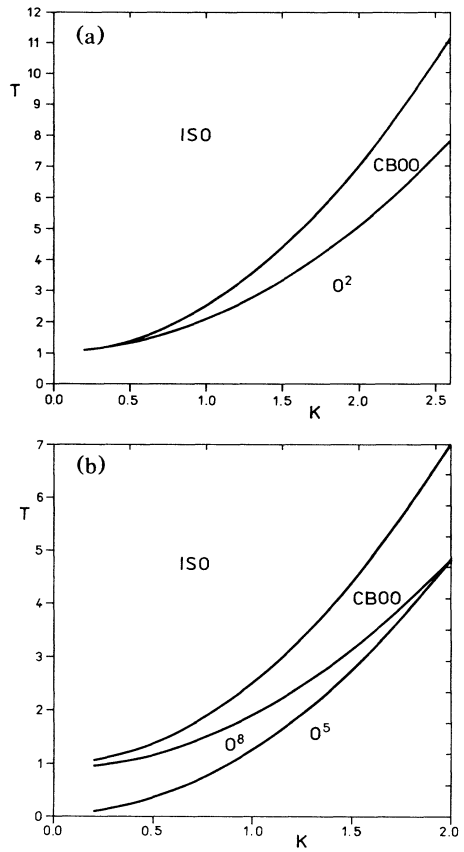

FIG. 1. Theoretical phase diagrams for $\tilde{a} = 1$, $\tilde{b} = 1.5$, $\tilde{\tau} = 0$, $c = 1$ when (a) all relevant cubic phases and the bond oriented phase (CBOO) are allowed, and (b) the $\mathcal{O}^2$ phase is not included.

orientational order. It accounts for the alignment of cubic blue phase crystallites by weak electric or magnetic fields [10]. It also rules out the artificial $\mathcal{O}^5$ structure of the standard theory [8] by selecting wave vectors which point into $[n00]$ directions. For a coupling parameter $\lambda > 0$ the $[n00]$ harmonics ($n = 1, 2$) of the order parameter expansion become dominant and enhance the stability of $\mathcal{O}^2$ and $\mathcal{O}^8$ structures with respect to $\mathcal{O}^5$. This again is in agreement with light scattering experiments in BPII, which show that the intensity of the [100] reflection dominates over the intensity of [110] reflexes. Finally, cubic bond ordering can arise before any space group symmetry becomes relevant. This implies that *the cubic bond oriented phase is a natural candidate for the structure of BPIII.* According to this model the translational order of BPI or BPII cubic lattices is lost in BPIII, but the system still remembers the orientation of crystallographic axes. Diffraction maxima should still be observed but there are no periodic planes to produce coherent Bragg diffraction. The position of a broad selective reflection band in BPIII, which is close to the [100] peak of BPII, again seems to be in favor of the present theory.

To test the predictions of this theory measurements of the nonlinear dielectric tensor $\bar{\varepsilon}_{\alpha\beta\mu\nu}$, *e.g., with the help of three-wave mixing*, are urgently needed.

This research was supported by the Heraeus Foundation and in part by the Polish Project No.2.0254.91.01.

* Present address: Department of Statistical Physics, Jagellonian University, Reymonta 4, Kraków, Poland. Electronic address: lech@zfs.if.uj.edu.pl

[1] For recent reviews see D. C. Wright and N. D. Mermin, Rev. Mod. Phys. **61**, 385 (1989); P. P. Crooker, Liq. Cryst. **5**, 751 (1989); R. M. Hornreich and S. Shtrikman, Mol. Cryst. Liq. Cryst. **165**, 183 (1988); V. A. Belyakov and V. E. Dmitrienko, Usp. Fiz. Nauk **146**, 369 (1985) [Sov. Phys. Usp. **28**, 535 (1985)].

[2] D. K. Yang and P. P. Crooker, Phys. Rev. A **35**, 4419 (1987).

[3] H. Stegemeyer and K. Bergmann, in *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke (Springer, Berlin, 1980), p. 161.

[4] M. Marcus, J. Phys. (Paris) **42**, 61 (1981).

[5] R. M. Hornreich and S. Shtrikman, Phys. Rev. Lett. **56**, 1723 (1986); see also H. Kleinert and K. Maki, Fortschr. Phys. **29**, 219 (1981).

[6] L. Longa, W. Fink, and H.-R. Trebin, Phys. Rev. E **48**, 2296 (1993).

[7] R. L. Rakes, Jr. and P. H. Keyes, Mol. Cryst. Liq. Cryst. **198**, 79 (1991); see also P. H. Keyes, Phys. Rev. Lett. **65**, 436 (1990);

[8] H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **28**, 1114 (1983); H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **30**, 3264 (1984); L. Longa, D. Monselesan, and H. R. Trebin, Liq. Cryst. **6**, 769 (1987).

[9] D. R. Nelson and J. Toner, Phys. Rev. B **24**, 363 (1981); P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. A **28**, 784 (1983).

[10] P. Pierański, P. E. Cladis, T. Garel, and R. Barbet-Massin, J. Phys. (Paris) **47**, 139 (1986).

[11] L. Longa and H. R. Trebin, Phys. Rev. A **42**, 3453 (1990).

[12] S. A. Brazovskii, I. E. Dzyaloshinskii, and A. R. Muratov, Zh. Eksp. Teor. Fiz. **93**, 1110 (1987) [Sov. Phys. JETP **66**, 625 (1987)].

[13] M. V. Jaric, Nucl. Phys. **B265**, 647 (1986).