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Experimental probes of bond orientational order models of blue phase III of chiral liquid crystals

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Recently, a cubic bond orientational order model was proposed for blue phase (BP) III [Phys. Rev. Lett. **71**, 2757 (1993)]. It was suggested that in blue phase III, although there is no periodic translational symmetry, a cubic orientational order persists. A spatially independent fourth-rank tensor $B^4_{\alpha\beta\mu\nu}$ was used to describe the cubic bond orientational order. In this paper, we show that since BP III is chiral, the bond orientational order parameter is expected to vary in space. Depending on the relative magnitudes of the elastic constants in the free energy, the cubic bond orientational order will twist along either a fourfold ([001]) or a threefold ([111]) symmetry direction. Due to the twist, the cubic symmetry of the bond orientational order is replaced by a lower point symmetry group, $D_4(422)$ or $D_3(32)$. Using Landau theory and dimensional analysis, we find that if there is a chiral cubic bond orientational order in BP III, there should be a measurable birefringence even in the absence of an external field. This is inconsistent with the knowledge that BP III is optically isotropic without a field. We also point out that a phase with cubic bond orientational order can be distinguished from an isotropic phase using field induced birefringence experiments.

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I. INTRODUCTION

Blue phases appear in chiral liquid crystals between either a helical (cholesteric) or smectic phase and the isotropic phase in a narrow temperature range. In the absence of an external field, three types of blue phases have been identified. It is believed that in blue phases I and II, the long axes of the molecules form periodic orientational patterns; blue phase (BP) I has the periodicity of a body-centered-cubic lattice and BP II has the periodicity of a simple cubic lattice. Sharp Bragg reflection bands of visible (often blue) light are observed in blue phases I and II. The structure of BP III, however, is still uncertain. It shows only a broad, weak selective reflection and no spatial periodicity is found. A number of models have been suggested for BP III. In general these models can be put into three categories: (1) quasicrystal models where the structure of BP III is characterized by the reciprocal-lattice vectors derived from the edges and vertices of an icosahedral [1, 2]; (2) amorphous models, which include double twist model [1, 2], where BP III is considered to be filled with randomly oriented double twist cylinders; emulsion model [1, 2] where BP III consists of cholesteric droplets; cubic domain model [1, 2] where small cubic domains predominate; and (3) the bond orientational order model, recently proposed by Longa and Trebin [3]. It was suggested that in BP III, although there is no translational periodicity as in blue phases I and II, a cubic bond orientational order remains. This last phase is described by two order parameters, the usual traceless symmetric alignment order parameter $Q_{\alpha\beta}(\vec{r})$ and a bond orientational order parameter, a fourth-rank tensor $B^4_{\alpha\beta\mu\nu}$ which results, for example, in new allowed tensors for the third-order nonlinear optical susceptibility.

In the cubic bond orientational order model, the free energy of the blue phases is written in terms of a mean-field free energy, which depends only on the alignment order parameter $Q_{\alpha\beta}(\vec{r})$, and a fluctuation part. The fluctuation part of the free energy is approximated by the free energy solely coming from the bond orientational order $B^4_{\alpha\beta\mu\nu}$ and its coupling to the alignment order parameter $Q_{\alpha\beta}(\vec{r})$. In particular, the contribution to the free energy from the bond orientational order alone is written as

$$\begin{aligned} F_{B,\mathrm{bulk}} = {} & a_2 B^4_{\alpha\beta\gamma\delta} B^4_{\alpha\beta\gamma\delta} + a_3 B^4_{\alpha\beta\gamma\delta} B^4_{\alpha\beta\mu\nu} B^4_{\gamma\delta\mu\nu} \\ & + a_{4,1} (B^4_{\alpha\beta\gamma\delta} B^4_{\alpha\beta\gamma\delta})^2 \\ & + a_{4,2} B^4_{\alpha\beta\gamma\delta} B^4_{\gamma\delta\mu\nu} B^4_{\mu\nu\rho\sigma} B^4_{\rho\sigma\alpha\beta}. \end{aligned} \tag{1}$$

In order to minimize the total free energy, $F_{B,\mathrm{bulk}}$ is minimized first using group theoretical techniques [4] and the cubic symmetry $O(432)$ for the bond orientational order parameter $B^4_{\alpha\beta\gamma\delta}$ is obtained. The total free energy is then minimized and it is found [3] that the $O^5(I432)$ structure is destabilized compared to the $O^2(P4_232)$ and $O^8(I4_132)$ structures, in contrast to the earlier analysis [2] without considering the bond orientational order. Also a purely bond orientational phase, in which $Q_{\alpha\beta} = 0$ and $B^4_{\alpha\beta\mu\nu} \neq 0$, can appear right below the isotropic phase where the BP III phase emerges.

For a nonuniform, spatially dependent, bond orientational order, $B^4_{\alpha\beta\gamma\delta}(\vec{r})$, there are other symmetry allowed terms in the bond orientational order part of the free energy, F_B, besides the bulk free energy, $F_{B,\mathrm{bulk}}$ of Eq. (1). One must also consider gradient terms, such as $\nabla_\alpha B^4_{\alpha\beta\gamma\delta} \nabla_{\alpha'} B^4_{\alpha'\beta\gamma\delta}$, $\nabla_\alpha B^4_{\beta\gamma\rho\sigma} \nabla_\alpha B^4_{\beta\gamma\rho\sigma}$, and $\epsilon_{\alpha\beta\gamma} B^4_{\alpha\rho\mu\nu} \nabla_\gamma B^4_{\beta\rho\mu\nu}$ (if not specified otherwise, summation on repeated indices is implied throughout this paper; $\epsilon_{\alpha\beta\gamma}$ is the commonly used antisymmetric tensor). Just as the gradient terms of the ordinary order parameter $Q_{\alpha\beta}(\vec{r})$ in the free energy introduce the helical phase, the additional gradient terms in the bond orientational order free energy lead to a chiral bond orientational order. Although it is known that the bond orientational order is not chiral in blue phases I and II, its chirality can manifest itself in BP III.

This is analogous to the well studied cholesteric to smectic A transition. In smectic A there is quasi-long-range translational order and there is no global twist associated with the chirality of the constituent molecules. This chirality is only exhibited in cholesteric phase. Recent theoretical analysis [5] of the similarity between the type II superconductors and the smectic A phase with chirality shows that there can be phase with smectic order and twist, the twist grain boundary phase. However this occurs only when the chirality is large enough. When the chirality is not that large the quasi-long-range translational order completely suppresses the twist of the order parameter. A few materials, such as nP1M7 and +14P1M7, have been confirmed experimentally [6] to exhibit the twisted grain boundary phase.

We find that the chiral cubic bond orientational order lowers the total bond orientational free energy, $F_B = F_{B,\mathrm{bulk}} + F_{B,\mathrm{grad}}$, comparing with the cubic bond orientational order in BP III. The twist direction of the cubic bond orientational order is either along [001] (one of the axes with fourfold symmetry) or [111] (threefold symmetry axis), depending on the relative magnitudes of the elastic constants. The chiral cubic bond orientational order is characterized by a symmetry lower than a cubic, such as the symmetry of the point group $D_4(422)$ or $D_3(32)$. This makes it plausible that the system will have a second-rank order parameter even without the influence of an external field. Using Landau theory and together with dimensional analysis to estimate the size of the phenomenological parameters, we find the chiral cubic bond orientational order induces a second-rank order parameter, and the system should be birefringent even without an external field, which contradicts the common knowledge that BP III is optically isotropic. We also propose to detect a possible cubic bond orientational order in BP III through a simple experiment, observation of the birefringence in a plane perpendicular to an applied weak field.

The paper is organized as follows. In Sec. II, we argue that in chiral systems with only orientational and not translational order parameters the order will be spatially dependent and through the analysis of the Landau theory we present the chiral cubic bond orientational order model. We then use the dimensional analysis to estimate the magnitude of the birefringence for both cubic and chiral cubic bond orientational order models with and without an external field. In Sec. IV we briefly review current available experimental results of BP III relevant to the bond orientational order models.

II. CHIRAL CUBIC BOND ORIENTATIONAL ORDER IN BP III

Blue phases appear only in chiral systems with short pitches so the system can be considered to be highly chiral. In such a system, the molecules tend to stack with their long axes at an angle relative to one another from point to point. Therefore the order parameter describing such a system should depend on spatial variables. For a spatially dependent bond orientational order parameter, additional gradient terms should be included in the free energy besides the terms in Eq. (1). In particular, for this bond orientational order parameter which transforms as the $l = 4$ irreducible representation of the SO(3) group, up to the second order in derivatives, the additional rotationally invariant terms quadratic in the order parameter are

$$\begin{aligned} F_{B,\mathrm{grad}} = \int d\vec{r}\,(&L_1 \nabla_\alpha B^4_{\alpha\beta\gamma\delta} \nabla_{\alpha'} B^4_{\alpha'\beta\gamma\delta} \\ &+ L_2 \nabla_\alpha B^4_{\beta\gamma\rho\sigma} \nabla_\alpha B^4_{\beta\gamma\rho\sigma} \\ &+ L_3 \epsilon_{\alpha\beta\gamma} B^4_{\alpha\rho\mu\nu} \nabla_\gamma B^4_{\beta\rho\mu\nu}), \end{aligned} \tag{2}$$

where the bond orientational order parameter $B^4_{\alpha\beta\gamma\delta}$ is a completely traceless symmetric fourth rank tensor,

$$\begin{aligned} B^4_{\alpha\beta\gamma\delta} = B[&{n^i}_\alpha {n^i}_\beta {n^i}_\gamma {n^i}_\delta \\ &- \tfrac{1}{5}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})], \end{aligned} \tag{3}$$

and $\hat{n}^i$ are the unit vectors along the three fourfold symmetry axes. In the chiral cubic bond orientational order model, parameter B is assumed to be a constant and $\hat{n}^i(\vec{r})$ (i=1,2,3) are varying in space. It is more convenient to express the gradient part of the bond orientational free energy, $F_{B,\mathrm{grad}}$, in terms of the gradients of the vectors $\hat{n}^i(\vec{r})$ [7],

$$\begin{aligned} F_{B,\mathrm{grad}} = \int d\vec{r}\{&\tfrac{1}{2}K_1(\nabla\cdot\hat{n}^i)^2 + \tfrac{1}{2}K_2[\hat{n}^i\cdot(\nabla\times\hat{n}^i)]^2 \\ &+ \tfrac{1}{2}K_3[\hat{n}^i\times(\nabla\times\hat{n}^i)]^2 + K\hat{n}^i\cdot(\nabla\times\hat{n}^i)\}. \end{aligned} \tag{4}$$

If derived from Eq. (2), the elastic constants K_1 and K_3 are equal, although they would be different if higher order terms were included. As we see below, our results are not affected by any relations between K_1 and K_3. One can easily evaluate the free energy associated with a twisted cubic bond orientational order using the above expression.

Suppose we choose the coordinate system such that the z axis is along the rotational axis and at $z = 0$, $\hat{n}^1$ is on the xz plane. In general, one can write

$$\begin{aligned} \hat{n}^1(\vec{r}) &= (\sin\theta_1\cos\phi(z), \sin\theta_1\sin\phi(z), \cos\theta_1), \\ \hat{n}^2(\vec{r}) &= (\sin\theta_2\cos[\phi(z)+\phi_2], \sin\theta_2\sin[\phi(z)+\phi_2], \cos\theta_2), \\ \hat{n}^3(\vec{r}) &= (\sin\theta_3\cos[\phi(z)+\phi_3], \sin\theta_3\sin[\phi(z)+\phi_3], \cos\theta_3), \end{aligned} \tag{5}$$

where $\phi(z)|_{z=0} = 0$ and θ_i, ϕ_i are spatially independent and they are related by orthogonal relations

$$\begin{aligned}
&\sin\theta_1\sin\theta_2\cos\phi_2+\cos\theta_1\cos\theta_2=0,\\
&\sin\theta_1\sin\theta_3\cos\phi_3+\cos\theta_1\cos\theta_3=0,\\
&\sin\theta_2\sin\theta_3\cos\phi_2\cos\phi_3\sin\theta_2\sin\theta_3\sin\phi_2\sin\phi_3+\cos\theta_2\cos\theta_3=0.
\end{aligned}\tag{6}$$

Eliminating ϕ_2 and ϕ_3 from the above relations, we find θ_i must satisfy equation

$$\sin^2\theta_1+\sin^2\theta_2+\sin^2\theta_3=2.\tag{7}$$

Substituting Eq. (5) into the free energy, Eq. (4), we can express $F_{B,\mathrm{grad}}$ in terms of θ_i and $\partial\phi/\partial z$,

$$\begin{aligned}
F_{B,\mathrm{grad}}=\int dz\Bigg\{&\frac{1}{2}K_2\left(\frac{\partial\phi}{\partial z}\right)^2(\sin^4\theta_1+\sin^4\theta_2+\sin^4\theta_3)\\
&+\frac{1}{2}K_3\left(\frac{\partial\phi}{\partial z}\right)^2(\sin^2\theta_1\cos^2\theta_1+\sin^2\theta_2\cos^2\theta_2+\sin^2\theta_3\cos^2\theta_3)\\
&-K\left(\frac{\partial\phi}{\partial z}\right)(\sin^2\theta_1+\sin^2\theta_2+\sin^2\theta_3)\Bigg\}.
\end{aligned}\tag{8}$$

Minimizing the above free energy using the constraints Eq. (6), we find that if the elastic constants satisfy $K_2 > K_3$, $F_{B,\mathrm{grad}} = -\Omega K^2/K_2$ (Ω is the bulk volume) is the smallest when $\theta_1 = \theta_2 = \theta_3 = \arctan\sqrt{2}$, which corresponds to a twist along a [111] direction with $\partial\phi/\partial z = K/K_2$; and if $K_2 < K_3$, $F_{B,\mathrm{grad}} = -3\Omega K^2/(2K_2 + K_3)$ is the minimum when $\theta_1 = 0$, $\theta_2 = \theta_3 = \pi/2$, which corresponds to a twist along a [001] direction with $\partial\phi/\partial z = 3K/(2K_2 + K_3)$.

Since $F_{B,\mathrm{bulk}}$ of Eq. (1) is rotationally invariant and has the same value for both the cubic and chiral cubic bond orientational order model, and $F_{B,\mathrm{grad}}$ is zero for the uniform cubic bond orientational order model but negative for twisted, chiral cubic bond orientational order model, the total bond orientational order free energy $F_B = F_{B,\mathrm{bulk}} + F_{B,\mathrm{grad}}$ is lowered if there is a twisted, chiral bond orientational ordering in the system. The fact that the additional gradient terms in the free energy lead to chiral bond orientational order is analogous to the well-known theory that the gradient terms of the ordinary order parameter $Q_{\alpha\beta}$ lead to a helical phase [1]. The magnitude of the expected pitch depends on the microscopic interpretation of the order parameter B. If B is a molecular orientational average, then it is reasonable to expect that the ratio of the chiral and elastic terms is comparable to that for the ordinary nematic order parameter so that the pitch of the chiral cubic bond orientational order in BP III should be comparable to the cubic lattice constant of the BP I and II, or around 10^3 [Å]. On the other hand, B could be related to a structure with a size approximately that of the cholesteric pitch. For example, if BP III is approximately BP II on short length scales so that lattice vectors can be identified locally, B might be the average of a fourth-rank tensor formed from such vectors. In this case, the chirality is very large (the unit cell of the BP II phase is highly chiral) and the length scale is the lattice spacing of the BP II phase so again the expected pitch of the bond orientational order parameter is of order the pitch of the nematic order parameter.

It is known that the BP I and II have periodic structures with cubic symmetry and therefore their underlying bond orientational orders also have cubic symmetry and there is no twist involved. However, this does not exclude the possibility of a twisted bond orientational order in BP III. It is easy to see that if the cubic bond orientational order is twisted along the [001] direction, the chiral cubic bond orientational order will have the symmetry of the point group $D_4(422)$; if twisted along the [111] direction, it will have the symmetry of the point group $D_3(32)$. This local decrease in symmetry is directly analogous to that in the cholesteric or chiral nematic which has $D_\infty(\infty 2)$ symmetry when nonchiral but $D_2(222)$ symmetry when twisted. Due to the breaking of the cubic symmetry, the bond orientational order parameter will result in finite expectation values for lower rank tensor order parameters, including the second-rank order parameter $Q_{\alpha\beta}$. We shall discuss this further in the next section.

III. EXPERIMENTAL PROBES OF THE BOND ORIENTATIONAL ORDER

In this section, we use the Landau theory to estimate the magnitude of the induced birefringence in the chiral cubic bond orientational order model. We also propose to identify possible cubic bond orientational order in BP III through the observation of birefringence under a weak field. Using the Kerr effect to distinguish the cubic bond orientational order has been previously proposed by Saidachmetov [7] for smectic D. Here we shall briefly discuss it in the context of BP III and use Landau theory and dimensional analysis to estimate the magnitude of the birefringence.

In the cubic bond orientational order model [3], BP III corresponds to a purely bond orientational phase where the alignment order parameter $Q_{\alpha\beta} = 0$ and $B^4_{\alpha\beta\gamma\delta} \neq 0$. Under the influence of an external field, however, just as the simple isotropic phase, there would be an induced second-rank order parameter $Q_{\alpha\beta}$ which couples to the field and this part of the free energy can be written as

$$F_Q = \Omega\lambda_0(Q_{\alpha\beta}Q_{\beta\alpha} - \lambda_1 Q_{\alpha\beta}[E_\alpha E_\beta]),\tag{9}$$

where λ_0 is introduced to simplify the dimensional analysis and it has dimensions of energy per unit volume with magnitude of $k_B T/\Omega$ (T is the room temperature and Ω is the bulk volume); λ_1 has the dimension of the third-order nonlinear optical susceptibility and is of the order [8] of 10^{-16} [m^2/V^2]. The induced order parameter $Q_{\alpha\beta}$ is the anisotropic part of the induced dielectric tensor, $Q_{\alpha\beta} = \epsilon_{\alpha\beta} - \epsilon_{\gamma\gamma}\delta_{\alpha\beta}/3$. In order to ensure that $Q_{\alpha\beta}$ is traceless and symmetric, tensors which couple to $Q_{\alpha\beta}$ in the free energy must also be traceless and symmetric. For example, if a tensor $T_{\alpha\beta}$ is coupled to $Q_{\alpha\beta}$, we include a term, $Q_{\alpha\beta}[T_{\alpha\beta}]$ in the free energy, where we define $[T_{\alpha\beta}] = (T_{\alpha\beta} + T_{\beta\alpha})/2 - \mathrm{Tr}(T)\delta_{\alpha\beta}/3$.

If the system is isotropic, one can easily minimize Eq. (9) and find that $\Delta\epsilon \approx 2n\Delta n \approx \Delta Q \sim AE^2$. With the field strength E of the order of 10^5 [V/m], the birefringence Δn is around 10^{-6}. One must keep in mind that the birefringence in isotropic systems can only be observed in a direction perpendicular to the applied field. If observed along the field direction, the system is still optically isotropic. We show in the following that if there is a bond orientational order, in general, the system is birefringent when observed *along* the field direction, which makes it easy to distinguish the bond orientational models from the amorphous models of BP III.

For systems with cubic bond orientational order under the influence of an external field, the total free energy includes F_Q of Eq. (9), $F_{B,\mathrm{bulk}}$ of Eq. (1), and the coupling terms among the bond orientational order parameter $B^4_{\alpha\beta\gamma\delta}$, the induced order parameter $Q_{\alpha\beta}$ and the external field, E,

$$F_{\mathrm{coupl,bulk}} = \Omega\lambda_0(\lambda_2 Q_{\alpha\beta}B^4_{\alpha\beta\gamma\delta}Q_{\gamma\delta} + \lambda_3 Q_{\alpha\beta}B^4_{\alpha\beta\gamma\delta}E_\gamma E_\delta). \tag{10}$$

The total energy for BP III of the cubic bond orientational order model is, therefore,

$$F_{\mathrm{tot,cubic}} = F_Q + F_{B,\mathrm{bulk}} + F_{\mathrm{coupl,bulk}}. \tag{11}$$

For chiral cubic bond orientational order, one needs to further consider additional gradient terms, such as

$$\begin{aligned} F_{\mathrm{coupl,grad}} = \lambda_0 \int d\vec{r}(&\lambda_4 Q_{\alpha\beta}[\epsilon_{\alpha\rho\eta}B^4_{\beta\sigma\mu\nu}\nabla_\rho B^4_{\eta\sigma\mu\nu}] \\ &+\lambda_5 Q_{\alpha\beta}[B^4_{\alpha\gamma\mu\nu}\epsilon_{\gamma\rho\eta}\nabla_\rho B^4_{\eta\beta\mu\nu}] \\ &+\lambda_6 Q_{\alpha\beta}[\nabla_\alpha B^4_{\eta\gamma\mu\nu}\nabla_\beta B^4_{\eta\gamma\mu\nu}]), \end{aligned} \tag{12}$$

and the total free energy is

$$F_{\mathrm{tot,chiralcubic}} = F_{\mathrm{tot,cubic}} + F_{B,\mathrm{grad}} + F_{\mathrm{coupl,grad}}. \tag{13}$$

In Eq. (12), we have assumed that $Q_{\alpha\beta}$ is spatially independent and we only included the lowest order nonzero terms which are at least first order in $Q_{\alpha\beta}$. The symbol [ ] which was defined earlier means that the tensor within the bracket has been made to be symmetric and traceless. Notice all the coupling terms which are first order in Q and B^4, such as $Q_{\alpha\beta}\nabla_\gamma\nabla_\delta B^4_{\alpha\beta\gamma\delta}$, $Q_{\alpha\beta}\epsilon_{\gamma\rho\sigma}\nabla_\gamma B^4_{\rho\sigma\alpha\beta}$, and $Q_{\alpha\beta}\nabla_\gamma\nabla_\gamma B^4_{\alpha\beta\mu\mu}$ are zero because $B^4_{\alpha\beta\mu\nu}$ of Eq. (3) is a symmetric and completely traceless fourth-rank tensor and B is assumed to be a constant. Surface terms such as $\int d\vec{r} Q_{\alpha\beta}\nabla_\rho B^4_{\alpha\gamma\mu\nu}\nabla_\rho B^4_{\beta\gamma\mu\nu}$ are also neglected.

In the preceding section we have shown that the bond orientational order part of the free energy $F_{B,\mathrm{bulk}} + F_{B,\mathrm{grad}}$ is minimized with a chiral cubic bond orientational order, with the chiral axis along either the [001] or [111] direction. We follow the standard procedure and assume this same bond orientational order would minimize the total free energy, $F_{\mathrm{tot,chiralcubic}}$. One can therefore obtain the induced order parameter Q by minimizing the total free energy, i.e., $\partial F_{\mathrm{tot,chiralcubic}}/\partial Q_{\alpha\beta} = 0$.

In the absence of an external field, from Eq. (11) it is obvious that $Q_{\alpha\beta} = 0$ for the cubic bond orientational order model. However, for the chiral cubic bond orientational order model, $Q_{\alpha\beta} \neq 0$, or there exists a bond orientational order induced birefringence. The magnitude of Q can be estimated by minimizing Eq. (13) with $\vec{E}$ set equal to zero,

$$\begin{aligned} 2AQ_{\alpha\beta} \; &+2\lambda_2 B^4_{\alpha\beta\gamma\delta}Q_{\gamma\delta} + \lambda_4[\epsilon_{\alpha\rho\eta}B^4_{\beta\sigma\mu\nu}\nabla_\rho B^4_{\eta\sigma\mu\nu}] \\ &+\lambda_5[B^4_{\alpha\gamma\mu\nu}\epsilon_{\gamma\rho\eta}\nabla_\rho B^4_{\eta\beta\mu\nu}] \\ &+\lambda_6[\nabla_\alpha B^4_{\eta\gamma\mu\nu}\nabla_\beta B^4_{\eta\gamma\mu\nu}] = 0. \end{aligned} \tag{14}$$

For the chiral cubic bond orientational model with chiral direction [001], for example, we find $Q_{11} = Q_{22} = -Q_{33}/2 = 5B^2(\partial\phi/\partial z)(\lambda_4 + 4\lambda_5 + 8\lambda_6\partial\phi/\partial z)/(10 + 6B\lambda_2)$. From Eq. (10), we see that λ_2 is dimensionless and has the magnitude of 1. As the transition is expected to be first order we expect that the bond orientational order parameter B is in the range of 0.2 to 0.4. Also from Eq. (12) we see that both λ_4 and λ_5 have units of length and, if B describes the *microscopic* order we estimate they have the magnitude of the characteristic length scale of the molecules, 10^{-9} [m]; λ_6 has the dimension of length squared, $\lambda_6 \sim 10^{-18}$ [m^2]. We expect that the pitch of the chiral cubic bond orientational order has the same order of the magnitude of the lattice constant of BP I and II, $(\partial\phi/\partial z) \sim 2\pi/P \sim 10^7$ [m^{-1}]. With these dimensional analyses, we therefore estimate that the birefringence $\Delta n \sim \Delta\epsilon \sim 0.1|Q_{11} - Q_{33}| \sim 10^{-4}$. If on the other hand B is associated with ordering on the scale of the cholesteric helix, that length is the typical length and the resultant birefringence should be much larger. In other words, the chiral bond orientational order induced birefringence is large enough to be easily detected in the absence of an external field.

Additionally for the cubic bond orientational order model, birefringence should be measurable under a weak field. Minimizing the total energy, $F_{\mathrm{tot,cubic}}$, we obtain

$$2Q_{\alpha\beta} - \lambda_1[E_\alpha E_\beta] + 2\lambda_2 B^4_{\alpha\beta\gamma\delta}Q_{\gamma\delta} + \lambda_3 B^4_{\alpha\beta\gamma\delta}E_\gamma E_\delta = 0. \tag{15}$$

If the field is along the [110] axis, $\vec{E} = (E, E, 0)$, for example, we find $Q_{11} = Q_{22} = -Q_{33}/2 = (5\lambda_1 - 3B\lambda_3)E^2/(30+18B\lambda_2)$ and $Q_{12} = (5\lambda_1 - 2B\lambda_3)E^2/(10 - 4B\lambda_2)$. It is easy to see that λ_3 in Eq. (10) has the same dimension as λ_1 in Eq. (9) with the magnitude of 10^{-16} [m^2/V^2], the birefringence observed along the field direction is therefore $\Delta n \sim 0.1|Q_{33} - |Q_{11} - Q_{12}|| \sim 10^{-7}$, assuming the field strength of the order of 10^5 [V^2/m^2]. Birefringence when the light is propagating along the field direction is symmetry forbidden in isotropic (e.g., amorphous) models of BP III. Birefringence of the order of 10^{-7} is experimentally observable. Note that as this system is known to have large scale chiral fluctuations which couple to light there should be appreciable and temperature or condition-dependent optical rotation, thus birefringence may be better observed through crossed (right and left) circular polarizers (rather than the more usual linear polarizers). Also when observation direction is perpendicular to the field direction, say along the z axis, with the same field strength, the birefringence is around $\Delta n \sim 0.2 Q_{12} \sim 10^{-6}$ and this is about the same order of magnitude as for the isotropic phase, discussed earlier.

Care must be taken in the birefringence measurement experiment. It is expected that if the sample is large enough (so surface effects do not dominate) and the sample is cooled from the isotropic phase, then the direction of the bond orientational order parameter will vary in space in complicated ways, rather as the nematic order parameter does with similar preparation. Through the analysis of the torque [9] and the free energy [7], it has been shown that depending on the sign of the parameter a in the expression for the nonlinear susceptibility tensor,

$$\chi^{(3)}_{\alpha\beta\gamma\delta} = a n_\alpha{}^i n_\beta{}^i n_\gamma{}^i n_\delta{}^i + b(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma}), \tag{16}$$

the system tends to rotate with the field such that the field direction is parallel to the [001] or [111] direction. It is easy to see using Eq. (15) that with such arrangements birefringence can only be observed perpendicular to the field direction, which makes it difficult to distinguish from an isotropic system. To avoid such a problem, one needs to limit the field strength well under a threshold so that the cubic bond orientation does not rotates with the field. For blue phases I and II, Pieranski *et al.* have estimated the critical field to rotate a free standing single crystal to be around 10^6 [V/m]. Since the surface also tends to reorient the ordering in BP III [10], the sample must be sufficiently thick so that one can observe the birefringence through the ordering of the bulk.

In summary, we find that if there is a chiral cubic bond orientational order in BP III, the system should be birefringent even in the absence of an external field. If there is a cubic bond orientational order in BP III, under a weak field, below the threshold of reorientation, one should be able to observe a birefringence along the field direction.

IV. SUMMARY AND DISCUSSION

Through the analysis of the Landau theory we propose a chiral cubic bond orientational order model for BP III, in which the cubic bond orientational orders found in BP I and II are twisted along either the [001] or [111] direction depending on the relative magnitudes of the elastic constants. The chiral cubic bond orientational model of BP III would yield a lower total bond orientational free energy comparing with the cubic bond orientational order model. Due to the twist, chiral bond orientational order has a symmetry lower than cubic, which implies that the system will have a finite expectation value for a second-rank order parameter. Landau theory predicts that there will be an order parameter $Q_{\alpha\beta}$ induced by the chiral bond orientational order even in the absence of an external field. We propose a simple experiment to observe possible birefringence along the field direction to distinguish the cubic bond orientational model from the amorphous models of BP III. This experiment should be considerably easier than the three-wave-mixing experiment proposed by Longa and Trebin [3].

We should stress that, like cholesteric, a blue phase with only orientational and not translational order will twist. Of course this does not change results for the crystalline blue phases which have translational order. However, it is interesting in this context to speculate that if orientational order in blue phases is important, there may, for large enough chirality (or weak enough translational order) be a phase like the twist grain boundary phase found in chiral smectic A. Such a phase would likely be birefringent, a reflection of the birefringence in the twisted bond orientational phase discussed above. There are some inconclusive experimental suggestions that this may occur [11]. It would also have an array of dislocations in the blue phase translational order which would result in additional Bragg peaks, likely close either to former Bragg peaks or the origin. A splitting of the [110] peak in BP II has been observed by Rakes and Keyes [12]. Such dislocations might also be observable in a photomicrograph; Sammon [13] has observed dislocation arrays induced by thermal gradients in this way.

It is worthwhile to review currently available experimental facts on BP III to further discuss the bond orientational models. Both cubic and chiral cubic bond orientational order models are consistent with the belief that there are some fundamental resemblances between BP III and BP II due to the small latent heat measured for the BP II–BP III transition. Recent light reflection experiments on BP III under an electric field reveal [14, 15] that for systems with negative dielectric anisotropy, there is a large increase of the intensity of the reflected light, while for systems with positive dielectric anisotropy, the intensity has little change or even decreases. Also for systems with either dielectric anisotropy there is not much shift of the wavelength corresponding to the intensity peak and the relaxation times in BP III are about three orders of magnitude shorter than those of the cubic blue phases. These are the indications that the mechanism in BP III under the influence of a field is not electrostriction of the blue phases I and II. By studying the linewidth of the reflected light as a function of the field strength, the experimental observations can be understood using the double twist model through the surface effects. It was suggested [15, 16] that the sample wall orders the sample to a penetration depth L_0 and the external electric field enhances the ordering and increases the penetration depth to $L > L_0$. Light incident on the sample is backscattered from the periodic modulation near the surface. With a simple model free energy of the form [15]

$$F = \frac{1}{2}[AQ^2 + B(dQ/dz)^2 - \chi Q^2 E^n], \tag{17}$$

where Q is a scalar order parameter which couples to the field E and z is the distance from the surface, it was found that the line shape and the intensity can be well fitted with the exponent $n = 2$. It was argued [15, 16] that in the absence of the field there must be a uniaxial component in the order parameter (anisotropic part of the dielectric matrix) in BP III which couples to the field as E^2. This essentially ruled out the models which have a cubic or icosahedral symmetry in the surface region. It is easy to see that if cubic structure dominates near the surface, the exponent on the external field in the free energy E^n would be $n = 4$. The reason is that there is no uniaxial component in the cubic order parameter; the induced order parameter $Q_{\alpha\beta} \sim E^2$ and its contribution to the free energy would be $Q_{\alpha\beta}E_\alpha E_\beta \sim E^4$. The strong correlation between the sign of the dielectric anisotropy of the system and the change of the reflection intensity are also successfully explained using the double twist model [15, 16].

Apparently in the cubic bond orientational order model, where the BP III is described as a purely bond orientational phase with the periodic mean-field alignment order parameter $Q_{\alpha\beta} = 0$, there is no order parameter which couples to the field as E^2. However, we have shown that the chiral cubic bond orientational order can induce a nonzero second-rank order parameter even without an external field. In this aspect that chiral cubic bond orientational order model seems to be more consistent with the recent experiments than the cubic bond orientational order model. However, the chiral cubic bond orientational order model expects the system to be birefringent in the absence of a field, which contradicts the common knowledge that BP III is optically isotropic.

There are quite a few experimental reports on the Kerr effects of BP I and II [10, 14]. Similar reports on BP III are still rare. We are not aware of any reports on the experiment we suggested in this paper, observation of the birefringence *along* the field direction in BP III. Singh and Keyes [8] have designed an experiment to directly detect the electric-field-induced birefringence by observing the samples *perpendicular* to the applied field. They found that the birefringence is proportional to the square of the field, both in BP III and in the isotropic phase, and there is almost no change of the birefringence from the isotropic phase to BP III. As discussed in the preceding section, when observation direction is perpendicular to the field, birefringence is expected to be the same order of magnitude in both the isotropic phase and the cubic bond orientational ordered phase. One cannot therefore justify or defy the existence of the bond orientational order in BP III from this experiment.

Overall, more experimental probes to the structure of BP III are certainly needed. Current available experimental facts seem to be more consistent with the amorphous model (such as the double twist model) than with the bond orientational models of BP III [17].

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