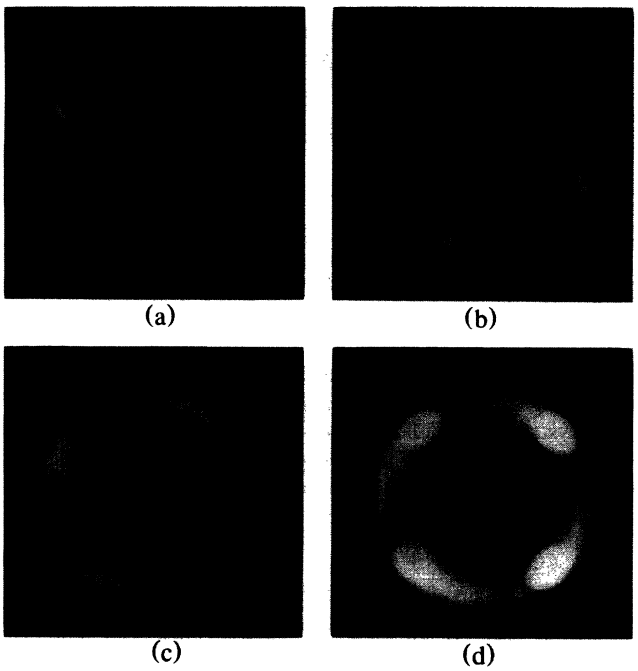

FIG. 1. Kossel diagrams of the [110] direction of BP-I as a function of increasing field strength. In (a)–(c) the wavelength is 529 nm and in (d) it is 496 nm. The field is applied in the [110] direction and the sample is 38 μm thick. (a) $V=0$ V, (b) $V=70$ V, (c) $V=V_c=90$ V, and (d) $V=100$ V.

cubic structure, $\xi_3=\xi_1$, as seen in Fig. 1(a). Finally, ξ_4 is defined in the following way. Each of the larger Kossel rings begins and ends on the boundary of the visible part of the focal plane. Draw a line joining these two end points. Then, ξ_4 is the angle between this line and a line parallel to ξ_1.

When an electric field is applied parallel to [110], the structure deforms so that ξ_1 no longer coincides with ξ_3 [Fig. 1(b)]. Finally, the fourfold pattern, shown in Fig. 1(c), announces the transition to the face-centered-tetragonal (fct) phase. The twofold [110] direction of the bcc lattice has transformed to the fourfold [001] direction of the fct lattice. To observe more lines in the fct phase, the wavelength is decreased [Fig. 1(d)]. If we reindex the lines relative to the fct lattice, [101] → [111], [011] → [$\bar{1}$11], etc. In Fig. 1(d), [200] → [202], etc., and [211] → [311] (one of the four bright spots), etc. There is, thus, a one-to-one correspondence between rings in the two phases. New rings do not appear, nor old rings disappear, at the transition. Figure 3(a) shows the evolution of the ξ's when a voltage is applied across a 38-μm-thick sample. ξ_1, ξ_2, and ξ_4 all show small discontinuities at the critical field $E_c=90$ V/(38 μm).

Blue-phase crystals are so soft so that, even for small fields, the unit cell deforms to gain electrostatic energy.[10] Kossel diagrams are a powerful tool for following the evolution of the unit cell in reciprocal space as a function

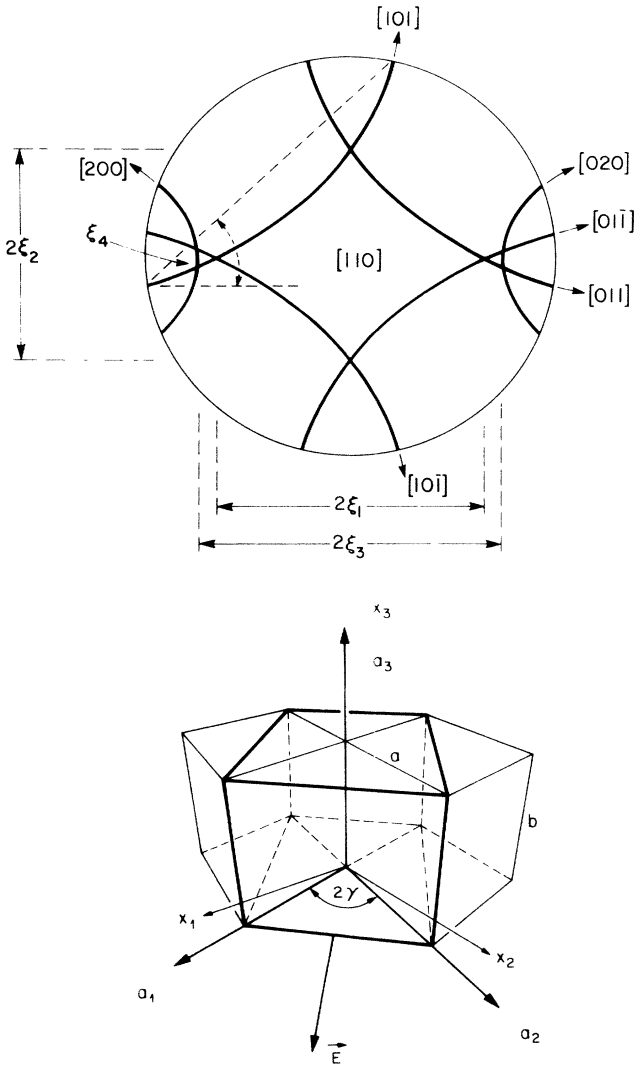

FIG. 2. Top: Definition of the ξ parameters measured from the Kossel diagrams. Bottom: Definition of structural parameters of the real-space unit cell.

of field. To relate these changes to the real-space lattice, we define the following bases vectors for a face-centered rectangular parallelepiped [Fig. 2(b)] with edges:

$$\begin{aligned}\mathbf{a}_1&=a(\cos[(\pi/4)-\gamma],\sin[(\pi/4)-\gamma],0),\\ \mathbf{a}_2&=a(\sin[(\pi/4)-\gamma],\cos[(\pi/4)-\gamma],0),\\ \mathbf{a}_3&=b(0,0,1).\end{aligned}\tag{1}$$

If $\gamma=\pi/4$, the $\mathbf{a}_i$ are bases vectors of a cubic unit cell that is bcc if $a/b=1$ and fcc if $a=b/\sqrt{2}$. When $\gamma\neq\pi/4$, the unit cell is orthorhombic if $2a\sin\gamma\neq b$ and tetragonal if $2a\sin\gamma=b$. Since twofold symmetry is observed [Fig. 1(b)] up to the transition [Fig. 1(c)], the field-induced deformation, described by the parameters, a, b, and γ, preserves the direction of $\mathbf{a}_3$ and the plane of $\mathbf{a}_1$ and $\mathbf{a}_2$. At constant volume, then, only two parameters, η_1

Kossel Diagrams Show Electric-Field–Induced Cubic-Tetragonal Structural Transition in Frustrated Liquid-Crystal Blue Phases

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Convergent beam diffraction patterns from a bcc blue-phase (I) monocrystal in an electric field applied in the [110] direction show this twofold axis transforming through an orthorhombic distortion to become, at a critical field, the fourfold axis of a tetragonal crystal. The implication on structures of blue phase I is important. Although the transition is weakly first order because the two order parameters describing it are coupled, the diffraction pattern changes continuously through the transition.

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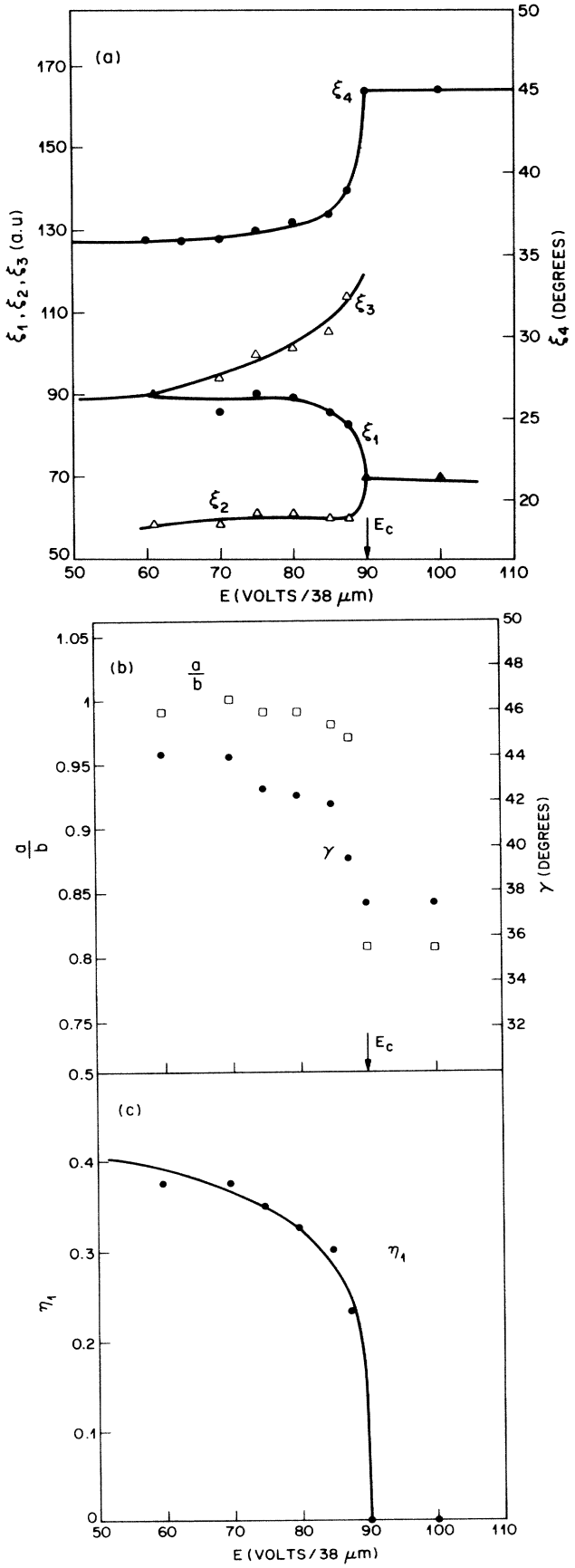
Blue phases (BP's) are an example of a condensed-matter system involving a network of defects.[1] They occur in a small temperature interval between the frustrated[2] cholesteric liquid-crystal phase and the isotropic liquid phase when the pitch is smaller than about 5000 Å. Cholesterics are frustrated because the *locally* favorable structure, called *double twist,*[3] is *globally* unfavorable. Blue phases are the compromise structures that relieve this frustration; thus their study is of substantial interest to the physics of the condensed state as a whole.[1]

The three blue phases,[1] BP-I, BP-II, and BP-III, are optically active but isotropic. The diffraction features of the BP (typically three sharp lines in the visible range for BP-I, two for BP-II, and one broad band for BP-III) and shapes of single crystals grown in contact with the isotropic liquid phase are consistent with a bcc [O^8 ($I4_132$)] structure for BP-I, a simple cubic [O^2 ($P4_232$)] structure for BP-II, and an amorphous or liquidlike structure for BP-III, also known as the blue fog. Kossel diagrams, single-crystal diffraction patterns formed by a converging light source,[4] confirm these assignments and provide quantitative information on blue-phase electric-field–induced structural transitions.[5–9]

Electric-field–induced structural transitions in blue phases were first considered by Hornreich, Kugler, and Shtrikman,[5] who predicted the hexagonal structure to be more stable in an electric field than the cubic structure in blue phases of cholesteric phases with positive dielectric anisotropy. This was recently confirmed by Pieranski, Cladis, and Barbet-Massin[6]; however, they observed more electric-field–induced structural transitions than just cubic to hexagonal. For example, in a 49.8% mixture of CB15 in E9,[6] the simple cubic phase of BP-II, oriented with its fourfold axis parallel to the field, transformed first to an unpredicted phase of tetragonal symmetry temporarily called BP-X, then to an unpredicted hexagonal phase where the c axis was a screw axis, then finally to the predicted hexagonal phase of Hornreich, Kugler, and Shtrikman.[5] These conclusions were based on observations of changes in the morphology of single crystals in contact with the isotropic liquid. More recently, Kossel diagrams of single crystals of these blue phases confirmed their symmetry in an unambiguous way[7] and led to the discovery of the bcc to tetragonal electric-field–induced transition in the BP-I phase of a 42.5% mixture of CB15 in E9 reported here.

Kossel rings are observed in the focal plane of the microscope objective. This is achieved by simple insertion of the Bertrand lens, standard equipment on most microscopes, or by removal of an eyepiece and insertion of a telescope to view the focal plane of the objective, when there is no Bertrand lens. The pattern of the rings gives direct evidence of the symmetry of a structure.[4,7] Figure 1(a), shows the typical pattern for a bcc crystal when the [110] crystal axis is along the direction of observation. The larger curves identified specifically in Fig. 2(a) are circular arcs of diffraction around the [011], [101], [01$\bar{1}$], and [10$\bar{1}$] poles. These poles and the diffraction ring around the central [110] pole are not observed since the angular aperture is too small and only part of the Kossel diagram is visible. The rings with the smaller radius of curvature are diffraction circles around the [200] and [020] poles, respectively. The pattern clearly shows the twofold symmetry of the [110] planes of a body-centered-cubic crystal.[4] Furthermore, these patterns are different for other cubic crystals.

Figure 2(a) shows the parameters ξ_i that we measure from the Kossel diagrams and relate to real-space lattice constants. In Fig. 1(a), the larger rings intersect at four points. $2\xi_1$ is the longer and $2\xi_2$ the shorter distance between two opposite intersection points [see Fig. 2(a)]. $2\xi_3$ is the distance between [200] and [020] rings. For a



$=2(a/b)\sin\gamma-1$, and $\eta_2\sim 2(a/b)\cos\gamma$, are needed to completely describe this deformation. η_1 describes changes in the a plane perpendicular to the field and η_2 measures changes in the direction of the field.

In terms of these parameters [Eq. (1)], we find that $\cot\xi_4=2(a/b)\sin\gamma=1+\eta_1\sim\xi_1/\xi_2$ and $\xi_3(E)=\xi_3(0)+\pi/4-\gamma$. Thus, γ is determined by measurement of ξ_3 in absolute units. ξ_4 measures the ratio of the two sides of the [110] face. For a bcc crystal $\cot\xi_4=\sqrt{2}$. We find $\cot\xi_4=1.43$ when $E=0$, within experimental error.

Figure 3(b) shows γ and a/b versus the voltage applied across a 38-μm sample as deduced from Fig. 3(a). In the figure, γ approaches the transition continuously whereas a/b is discontinuous.

The tetragonal-orthorhombic transition can be completely described in terms of two elastic order parameters[11] η_1 and η_2 defined above and, in general, by components of a deformation tensor e_{ij} of the tetragonal unit cell. When z is parallel to the fourfold axis, $\eta_1=e_{xx}-e_{yy}$ and $\eta_2=e_{xx}+e_{yy}-2e_{zz}$. In the tetragonal phase, $E>E_c$, $\eta_1=0$. At E_c the 422 (D_4) point symmetry of the tetragonal phase is broken and replaced by the 222 (D_2) point symmetry of the orthorhombic phase so that $\eta_1\neq 0$. The free energy F_1 is even in η_1 by symmetry:

$$F_1=\alpha\eta_1^2+\beta_0\eta_1^4+\cdots. \tag{2}$$

At E_c, $\alpha=0$. Here the analog of temperature is E and α is the elastic constant $(C_{11}-C_{12})/4$. The energy to distort the unit cell in the direction parallel to the field is

$$F_2=F_0+(1/2\chi)\eta_2^2. \tag{3}$$

Here, $1/2\chi$ is the elastic constant $(C_{11}+C_{12}-4C_{13}+2C_{33})/9$. Because η_2 is an invariant of the 422 point group, there is a coupling between the two order parameters, η_1 and η_2, that to lowest order is of the form

$$F_{12}=-\Gamma\eta_1^2\eta_2,\quad \Gamma>0. \tag{4}$$

The total energy, $F=F_1+F_2+F_{12}$, is now seen to be identical to the familiar[12] nematic-smectic-A transition when the layer order parameter ψ is coupled to the orientational order parameter S, or the Bean-Rodbell magnetic transition where magnetization is coupled to lattice deformations.[13] In our case, η_1 is analogous to ψ/magnetization and η_2 to S/lattice deformations. As de Gennes has shown,[12] the presence of F_{12} renormalizes the coefficient of the fourth-order term to $\beta=\beta_0-\chi\Gamma^2/2$. Thus, β may be negative for large enough χ and Γ.

A negative β, of course, means that the transition is first order and higher-order terms must be included in

FIG. 3. (a) Variation of the k-space structural parameters as a function of the electric field. (b) Variation of the real-space structural parameters as a function of electric field. (c) Variation of the elastic order parameter, η_1, as a function of electric field.

Eq. (2). Bean and Rodbell[13] have explicitly calculated a parameter proportional to $1-\beta$. By comparison of the variation with field of $\eta_1=\cot\xi_4-1$ in Fig. 3(c) with their theoretical estimates for the magnetization as a function of temperature, the tetragonal-orthorhombic transition seems weakly first order. β is slightly negative or the Bean-Rodbell parameter is about 1.3.

The occurrence of the tetragonal phase has the following important implication on BP-I structures. While the fundamental idea[2,3] that double twist relieves cholesteric frustration is indisputable, detailed models with extended objects like double-twist cylinders threading many unit cells[14] may not be the building block of BP-I. The reason is that an O^8 model built of rigid double-twist cylinders does not have tetragonal symmetry when deformed in the way we just described. Under such a deformation, its twofold axis remains a twofold axis.

Additional evidence that the structure has indeed undergone a phase transition to the tetragonal phase is found when the fct monocrystal transforms back to the distorted cubic phase. When the field is decreased to below E_c, in general, domains separated by grain boundaries corresponding to *both* signs of η_1 occur. One domain may eventually be favored and a bcc monocrystal is again recovered.

In conclusion, using Kossel diagrams, we showed that an increasing electric field applied parallel to the [110] direction of a bcc monocrystal of BP-I transforms this twofold axis into the fourfold axis of a face-centered-tetragonal crystal at a critical field. The transition is characterized by a continuous deformation of the unit cell but is weakly first order because of a Bean-Robbell coupling between the two order parameters describing the transition. Although weakly first order, the Kossel rings evolve continuously through the transition. This implies that the network of defects in the bcc phase is continuously transformable to the network of defects in the tetragonal phase. Since there is no way to deform an O^8 arrangement of rigid double-twist cylinders in a way that the twofold axis of the bcc crystal becomes the fourfold axis of the tetragonal crystal, they may not be the basic building block of BP-I. Other double-twist structures must be found.

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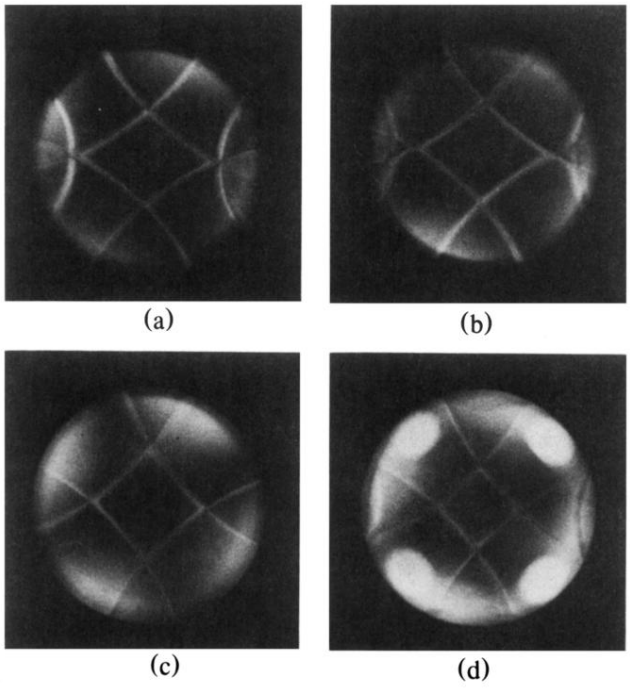

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