collection itself did not cause the observed oscillations near ω_{pi}: (1) The wave train did not change with change in positive bias of the probe; (2) exciting the probe with a potential step caused no oscillations in the electron current.

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ELECTRIC-FIELD-INDUCED COLOR CHANGES AND PITCH DILATION IN CHOLESTERIC LIQUID CRYSTALS

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A new electric-field–induced color range, in which colors change from blue to red with increasing field, has been observed in cholesteric liquid crystals. Observations of this new color range quantitatively confirm the theories of Meyer and de Gennes and enable identification of the specific nature of the electric-field–induced cholesteric-nematic phase transitions previously observed by other workers.

Introduction.—The dramatic color changes resulting from the application of electric fields to cholesteric liquid crystals have been well known since the initial investigations of Fergason and Harper.[1] However a theoretical basis for these effects has yet to be quantitatively confirmed.

Recently Meyer[2] and de Gennes[3] calculated the effects of external electric[2] and magnetic[2,3] fields on the helical structure of cholesteric materials. For the magnetic field case their predictions have been verified by the experiments of Durand *et al.*[4] and Meyer.[5] Although the electric-field–induced cholesteric-nematic phase transitions predicted by Meyer have been observed by Wysocki, Adams, and Haas[6] and by Baessler and Labes,[7] until the current investigation, the specific nature of these experimentally observed transitions has remained uncertain.[8]

We report here the observation of a new electric-field–induced color range, different from that reported by Harper and other previous workers. In this new color range, colors change from *blue to red* with increasing electric field for fields applied *normal* to the helical-ordering axes. In contrast, the effects observed by Harper change from *red to blue* with increasing field and have been generally attributed to fields applied *parallel* to the helical-ordering axes.[1] The new color-change region enables us to observe the details of the cholesteric-nematic pretransition phenomena and thereby to identify the specific nature of this phase transition. These observations quantitatively confirm the theories of Meyer and de Gennes for the influence of electric fields applied normal to the helical-ordering axes.

Also reported here are observations of electric-field–induced 90° reorientations of the helical-ordering axes. Finally, certain transient phenomena are briefly considered.

Sample preparation.—The mixed crystal system composed of cholesteryl chloride (CC), cholesteryl nonanoate (CN), and cholesteryl oleyl carbonate (COC) was chosen for this investigation because it orders cholesterically at room temperature, at which all measurements were made, with a convenient range of pitches determined by the relative concentrations of the individual components. All component materials were obtained commercially and used without further purification.[9] Three samples (I, II, III) with zero-field pitches $p_0 \approx (2330, 3400, 7400$ Å) and consisting by weight of CC (30.0, 37.5, 48.05 %), CN (28.0, 25.0, 20.9%), COC (42.0, 37.5, 31.05%) were prepared by heating the materials to 90°C, mixing them mechanically without solvent, and allowing them to cool slowly to room temperature.

Fields were applied to the samples by sandwiching them between transparent electrodes of SnO_2 deposited on glass and separated by a 6-μ-thick Mylar spacer with a 5-mm-square window cut for the sample. The sample package was given mechanical stability by clamping with alligator clips. Typical sample resistivities were on the order of 10^{13} Ω cm. Because of uncertainty in the actual sample thickness as a result of material viscosity and small deformations of the cut edges of the Mylar spacer, the quoted field values should be regarded as only approximate. However, because our principal results are independent of sample thickness, more precise dimensional measurements were not undertaken.

Direct visual observations.—Before voltage was applied, all samples were optically clear and optically active. Sample I, the only one with appropriate pitch ($2np_0 \approx 7000$ Å), showed strong colored scattering, i.e., dispersive reflection, with maximum intensity when viewed from near the specular direction. Sample II scattered only very faintly, and sample III not at all. For sample I, the variation of color with viewing and illumination directions qualitatively followed the relation[10]

$$\lambda = 2np\cos\tfrac{1}{2}[\sin^{-1}(n^{-1}\sin\varphi_i) - \sin^{-1}(n^{-1}\sin\varphi_s)] \qquad (1)$$

which was derived for Bragg scattering from a material with pitch p and average index of refraction n, where λ is the optical wavelength in free space, φ_i the angle of incidence, and φ_s the angle of observation, as shown in Fig. 1(a). We use the convention that φ_i and φ_s have opposite signs when on opposite sides of the normal.

At applied fields typically on the order of 2×10^4 V/cm all the samples became cloudy and presented a macroscopic appearance superficially resembling that of dynamic scattering.[11] On a microscopic scale, the material consisted of domain-like birefringent regions.[12] The principal results of this research relate to the internal structure of these birefringent regions.

With the appearance of these birefringent regions, the colored scattering of sample I disappeared. However, when the field applied to sample I was increased to about 2.6×10^5 V/cm, strong colored scattering could be observed when the sample was viewed from near the direction of the incident light. With further increases in voltage the color of the scattered light shifted from blue to red. Finally at about 3×10^5 V/cm the birefringent domains disappeared, and the sample became clear.

To our knowledge the field-induced color range described above has not been previously observed. The scattering in this new color range no longer follows Eq. (1) but instead qualitatively obeys the relation[13]

$$\lambda = 2np\sin\tfrac{1}{2}[\sin^{-1}(n^{-1}\sin\varphi_i) + \sin^{-1}(n^{-1}\sin\varphi_s)]. \qquad (2)$$

In contrast to the initial zero-field scattering, no colors are observable in the specular direction.

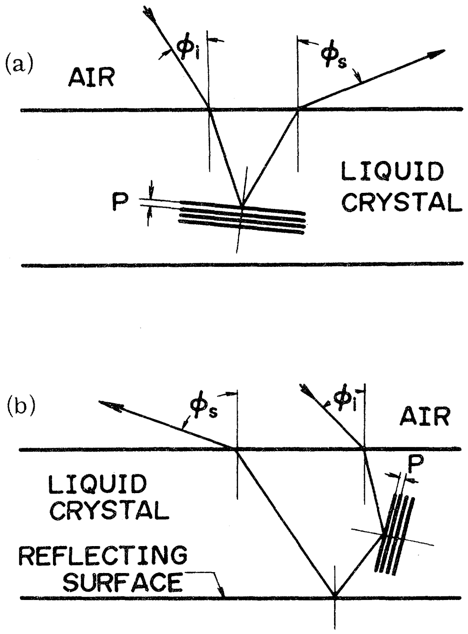

FIG. 1. Geometry for Bragg scattering from cholesteric liquid crystals. (a) Appropriate geometry for helix axes approximately normal to the sample surface. (b) Appropriate geometry for helix axes approximately parallel to the sample surface.

As electric fields were reduced, the same general phenomena were observed in reverse order except that the effects of hysteresis were important or even dominant in some regions. Once they had been established, the birefringent domains tended to persist even at zero field. In the longer pitched samples II and III, the new color range was observable down to zero field once the birefringent domains had been established. Electric-field-induced clearing was also observable in these samples, but at somewhat different field values than in sample I.

Interpretation.—Adams, Haas, and Wysocki[13] have shown that two states of order may be distinguished in cholesteric liquid crystals at zero field. They call these states disturbed and undisturbed because the transition from one to another may be caused by a mechanical disturbance. In the disturbed (undisturbed) state the helical-ordering axes tend to be aligned normal (parallel) to the sample surface; Bragg scattering processes occur as illustrated in Fig. 1(a) [Fig. 1(b)]; and the scattering is described by Eq. (1) [Eq. (2)].

The zero-field observations of the current investigation correspond to the disturbed state which is often called the planar or Grandjean texture, and the new color-change region induced by the electric field corresponds to the so-called undisturbed state. Thus, in a sense, the electric field causes the disturbed material to revert to its undisturbed state. Referring to Fig. 1(b) we note that according to this model the new color-change region would not be observable in reflection unless the lower electrode were at least partially reflecting. Confirmation of the model was obtained by substituting a highly reflecting Al electrode for the weakly reflecting SnO_2 lower electrode. As expected, a large increase in the Bragg scattering intensity resulted.

A quantitative explanation of the new color-change region follows from arguments originally advanced by Meyer.[2] Define a unit vector $\hat{L}$ which is parallel to the axis of molecular alignment at any point in the sample. Suppose that initially at zero field the boundary conditions make it energetically favorable for $\hat{L}$ to be parallel to the electrode surfaces. Then if the molecular ordering is described by the uniform helix $\hat{L} = (\cos t_0 z,\ \sin t_0 z,\ 0)$, the helix axis, $\hat{z}$ direction, will be normal to the electrodes. This is the planar texture observed at zero field.

If $\chi_p > \chi_t$, where χ_p and χ_t are the electric susceptibilities parallel and perpendicular to $\hat{L}$, respectively, then a sufficiently high electric field will tend to reorient the material into domains with helix axes 90° to the original state, i.e., in the plane of the sample. This process corresponds to the creation of birefringent domains and the resultant destruction of the planar texture reported above for threhold fields on the order of 2×10^4 V/cm.

As the field is further increased, Meyer has shown that the helical structure will be distorted and its spatial periodicity will increase. De Gennes[3] has carried out the full calculation for the magnetic field case. Although de Gennes has not so indicated, his computations apply equally well to the electric field case and result in the predicted variation of pitch with electric field given by the solid curve in Fig. 2. As the field increases, the pitch increases logarithmically until at a critical field given by $E_c = (\pi^2/p_0)[k_{22}/(\chi_p - \chi_t)]^{1/2}$, where p_0 is the pitch at zero field and k_{22} is an elastic modulus for the liquid crystal, the pitch becomes infinite; i.e., all molecules are aligned parallel, thereby corresponding to either a nematic or a smectic state.

The region of variable pitch resulting from electric fields applied normal to the helical-ordering axes corresponds to the new color-change region reported here. Similarly, the critical field predicted by de Gennes corresponds to the clearing of the sample observed at fields on the order of 3×10^5 V/cm for sample I. Quantitative confirmation of this model was provided by the following Bragg scattering experiment.

Bragg determination of pitch versus electric field.—For the special case $\varphi_i = \varphi_s$, Eq. (2) reduces to the simple relation

$$\lambda = 2p \sin\varphi_i, \tag{3}$$

which no longer depends on the index of refraction. For the case of Eq. (3) and a source of fixed wavelength (6328 Å), the pitch is readily determined by measuring the angle φ_i at which maximum scattering is observed. Use of an Al mirror as the lower electrode further simplifies the experimental geometry, making it necessary to rotate only the sample.

The sample was mounted with its surface parallel to the axis of rotating stage, and the scattered signal was detected in the backward direction by means of the half-mirror arrangement shown in Fig. 3. For improved sensitivity the incident light was chopped at about 1 kHz, and the signal was synchronously detected. In this manner scattering angles were measured with relative ease in the range $10° \leq \varphi_i \leq 70°$ and to an estimated accuracy of about ±0.3°.

The experimentally determined dependence of pitch on electric field for samples II and III is plotted in Fig. 2. The quantitative agreement with the theoretical curve confirms both the mod-

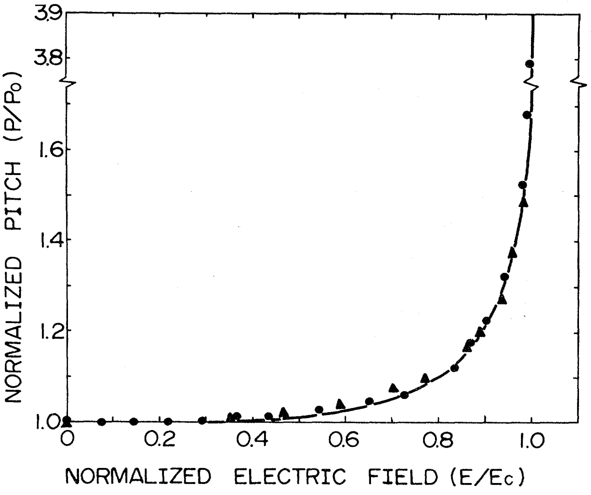

FIG. 2. Helix pitch p versus applied electric field E. Experimental results are for sample II (circles) and sample III (triangles) with p_0 approximately 3400 and 7400 Å, respectively; theoretical curve is after de Gennes (see Ref. 3). Critical field E_c is that for cholesteric-nematic phase transition.

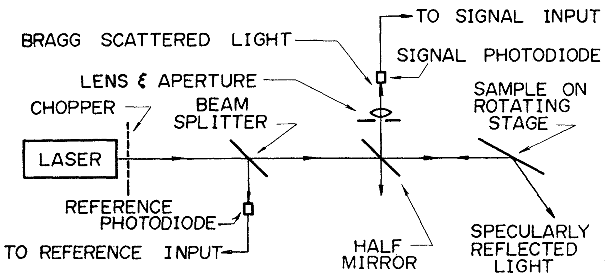

FIG. 3. Schematic diagram of Bragg spectrometer for determination of pitch versus electric field. For details see text.

el presented here and those of Meyer and de Gennes for field-induced cholesteric-nematic phase transitions.

Transient phenomena.—Transient phenomena are also being investigated and more detailed results will be reported elsewhere. However certain preliminary results are quoted here.[14]

Using the Bragg spectrometer of Fig. 3, it has been possible to observe the helix reorientations and the field-induced buildup of the birefringent domains separately from the pitch dilations. For example, suppose disorder is induced in sample III by exciting it into the nematic state with $E > E_c$ followed by quenching to zero field by means of a short circuit. Then Bragg scattering reappears with characteristic rise times of 2-4 min when electric fields of appropriate strength are applied. However, once the birefringent domains have been established, the new texture can remain at zero field for hours, days, or even longer, depending on the sample.

On the other hand, the response times associated with the pitch distortions and dilations can be orders of magnitude shorter. In fact rise and fall times of 1 and 2 msec, respectively, have been observed in unpolarized white light for the response of sample I to voltage pulses superposed on a suitable dc bias. These transient responses hint of a possibly bright future for the new color range in device applications.

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