Field-induced optical biaxiality in chiral smectic-*A* liquid crystals

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Observation of field-induced optical biaxiality in a chiral smectic-*A* liquid crystal is reported for the first time. Optical transmission measurements as a function of electric field demonstrate that a material exhibiting a large electroclinic effect also exhibits a pronounced optical biaxiality. It is shown that the biaxiality is correlated with the electroclinic tilt angle and its field dependence can be qualitatively explained in terms of a simple molecular model involving reorientation about the long molecular axis. [S1063-651X(97)50102-4]

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Smectic liquid crystals composed of chiral molecules are important electro-optical materials, whose physical properties depend strongly on the degree of order in these mesomorphic phases. In general, the smectic-*A* and smectic-*C* phases are orientationally ordered fluids with a density modulation or layering in one dimension and liquidlike molecular arrangement in the other two dimensions. In the smectic-*A* (Sm-*A*) phase the molecules within a layer are, on the average, parallel to the layer normal, while in the smectic-*C* (Sm-*C*) phase they are uniformly tilted. In addition to molecular tilt, the dielectric biaxiality of the Sm-*C* phase also distinguishes it from the uniaxial Sm-*A* phase, as demonstrated experimentally [1,2]. When the constituent molecules are chiral, the resultant chiral smectic-*C** (Sm-*C**) phase has no mirror symmetry and exhibits macroscopic polarization.

The chiral Sm-*A** phase is particularly interesting. In the absence of an electric field, the molecules are free to rotate about their long axis, and the Sm-*A** phase is uniaxial even though the molecular environment is monoclinic. When an electric field **E** is applied parallel to the smectic layers, this free rotation is restricted, since the transverse component of the permanent molecular dipole **P** tends to align with the field, resulting in a tilt of the molecule within the layer. This effect, known as the electroclinic effect, was first observed and explained in terms of symmetry by Garoff and Meyer [3], and has since been the object of intensive investigation [4,5]. The symmetry-breaking tilt of Sm-*A** should be accompanied by field-induced biaxiality [6], which, like the electroclinic effect, arises from the interaction of the applied field with the transverse dipole moment of the molecule.

The extent to which field-induced biaxiality affects the optical response of the Sm-*A** phase is not well understood. Although field-induced dielectric biaxiality [7] has been reported at low frequencies for Sm-*A** liquid crystals, the optical analog of this effect has not been observed so far. In fact, such an observation is not necessarily a foregone conclusion [8] in view of the fact that strong electric-dipole contributions play little role at optical frequencies and that the naturally tilted smectic-*C** phase is frequently regarded as optically uniaxial [6,9] even when the biaxiality at low frequencies is large [1,2]. A critical examination of optical biaxiality is needed for a fundamental understanding of the electro-optic response in the Sm-*A** phase. Further, the nature of the biaxial order, its field dependence and precise relation to electroclinic tilt remain to be elucidated.

In this Rapid Communication, observation of field-induced optical biaxiality in a chiral smectic-*A* phase is reported. By measuring the optical transmission as a function of polarization angle and electric field, it is shown that a material exhibiting a large electroclinic effect also exhibits a pronounced optical biaxiality. It is further shown that the biaxiality is correlated with the electroclinic tilt and its field dependence can be qualitatively explained in terms of a simple molecular reorientation model.

The liquid crystal material, denoted as KN125, has a structure shown in Fig. 1, and possesses the following phase sequence: crystal−(33 °C)−chiral Sm-*A*−(78 °C)−isotropic. Bipolar, square-wave electric fields were applied across the temperature-controlled cells, which are similar to those described in an earlier work [10]. Their thicknesses (10–20 μm) were determined from interference fringes. The measurement geometry is also illustrated in Fig. 1. The homogeneously aligned chiral smectic-*A* liquid crystal is in the bookshelf geometry, the smectic layers being perpendicular to the cell windows responsible for surface alignment. Application of the electric field causes the molecular director $\hat{\mathbf{d}}$ to rotate through an angle θ (the electroclinic tilt angle) relative to the smectic layer normal $\hat{\mathbf{n}}$, in a plane perpendicular to the electric field. We define a tilted coordinate system (X_L, Y_L, Z_L) whose Z_L axis lies in the plane normal to **E** but is rotated by an angle θ with respect to the smectic layer normal so as to coincide with the molecular director $\hat{\mathbf{d}}$. The Y_L axis is normal to the cell windows and parallel to the electric field, and X_L is orthogonal to Y_L and Z_L.

The transmission of an optical beam propagating along Y_L is measured as a function of light polarization angle for a series of applied voltages with the sample between either crossed or parallel polarizers. For crossed polarization, the transmitted signal is given by [11]

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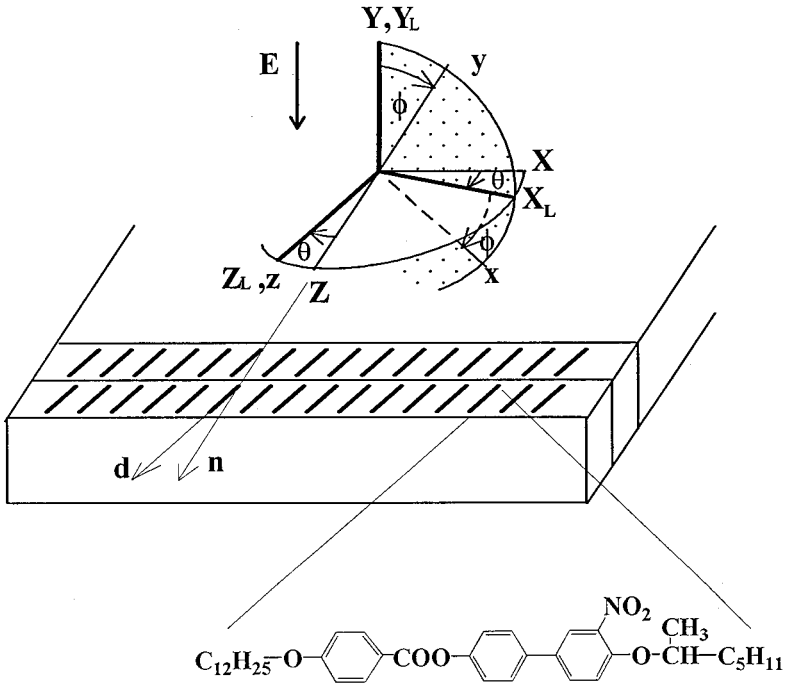

FIG. 1. The measurement geometry, illustrating the rotated laboratory coordinated frame (X_L, Y_L, Z_L), obtained from the sample coordinates (X,Y,Z) by a θ rotation about the Y axis, and the molecular frame (x,y,z) obtained by a ϕ rotation about the Z_L axis. The molecular structure of KN125 is also shown.

$$I_{\perp} = I(0)\sin^2(2\alpha)\sin^2(\psi/2). \quad (1)$$

Here, α is the angle between the polarization vector and the molecular director, $\psi = 2\pi\Delta n d/\lambda$ is the phase angle, and the birefringence, $\Delta n \equiv n_{Z_L} - n_{X_L}$, is the difference in refractive indices for light polarized along the Z_L and X_L axes. The variation of the electroclinic tilt angle θ (and hence α) with electric field causes a shift in the angular position of the maxima and minima. Any change in the value of the transmission maximum would indicate a field-dependent birefringence Δn.

Figure 2 illustrates the measured transmission as a function of an applied field and angular orientation of the sample relative to that of the crossed polarizers. The experimental dependence of the transmitted signal on angle varies systematically as the electric field varies from 0 (lowest curve) to 10.5 V/μm (highest curve). Two prominent features should be noted: (i) the variation in the angular positions of the transmission minima and maxima, from which $\theta(E)$ may be determined, and (ii) the change in the amplitude of the transmission maximum. As shown in Fig. 3(a), θ initially increases rapidly with electric field, but saturates at higher fields. Tilt angles as high as 15° were measured, consistent with results reported earlier for KN125 [10].

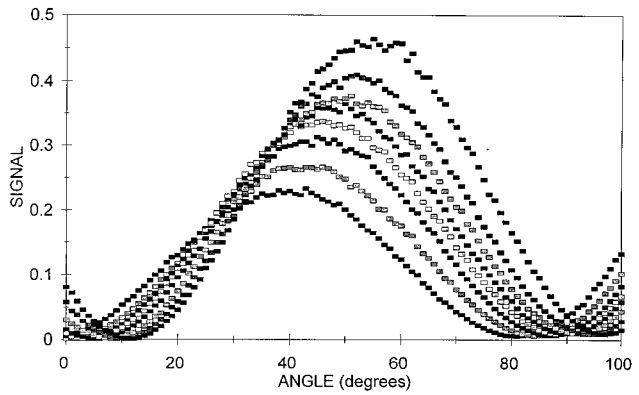

FIG. 2. Crossed-polarized transmission as a function of polarization angle for KN125, subjected to electric fields of 0.0 V (lowest data set), 1.0 V/μm, 2.1 V/μm, 3.1 V/μm, 4.2 V/μm, 5.2 V/μm, 7.3 V/μm, and 10.5 V/μm (highest data set).

It should be noted that large electroclinic tilt angles also induce strain, since they tend to decrease the local smectic layer spacing which is constrained at the alignment surface. The resulting deformation of the bookshelf geometry can be shown to reduce the magnitude of the crossed-polarized transmission maximum by no more than a few percent [10]. This deformation may be safely ignored here, since the predicted change in transmission is over an order of magnitude too small, and is of the wrong sign (see Fig. 2). A detailed discussion of this deformation in KN125 will be the subject of future work.

The magnitude of the crossed-polarized transmission maxima doubles between 0 and 10.5 V/μm, indicating a field-dependent Δn. This is, to our knowledge, the first observation of field-dependent birefringence in smectic-A^* liquid crystals. Note that the effect of this variation in Δn on the electro-optic response is comparable in magnitude to that of the electroclinic tilt. The experimental transmission data for various samples were fit using Eq. (1), and Δn was determined as a function of an applied field. Figure 3(b) shows the field dependence of $\delta\Delta n(E) \equiv \Delta n(E) - \Delta n(0)$ for a 10-μm-thick sample. The rapid increase in birefringence at the lowest fields and subsequent saturation at the highest fields are similar to the observed field dependence of the electroclinic tilt angle. At the highest fields, the measured values of $\delta\Delta n$ represent a several percent change in Δn, which varies from 0.14 to 0.16 across the visible spectrum. The variation in Δn could in principle be related to either a change in n_{X_L}, arising due to field-induced biaxiality, or a change in

n_{Z_L} [12]. The latter could arise, for example, if the field were to deform the liquid crystal so that the long molecular axis, and hence the largest axis of the refractive index ellipsoid, no longer lies in the plane normal to the electric field (i.e., the X_L-Z_L plane). This in turn would lead to a decrease in n_{Z_L} and therefore Δn, contrary to our experimental observations [Fig. 3(b)] which show Δn increasing with increasing field strength [13]. An increase in Δn is in fact what would be expected for field-induced biaxiality. From the molecular structure shown in Fig. 1, the larger of the two minor axes of the polarizability and hence refractive index ellipsoid is expected to be along the transverse component of the dipole moment. Therefore, the electric field tends to align the larger of the two axes in the Y_L direction, causing n_{X_L} to decrease and Δn to increase. It is thus clear that the observed increase in Δn for this surface stabilized smectic-A^* liquid crystal arises from field-induced biaxiality.

To relate these experimental results to molecular parameters, we assume that all molecules have their long axes aligned along Z_L, and that their azimuthal orientation is described by some angular distribution function. Hence, we define the molecular coordinate system (x,y,z), where $z = Z_L$, and x and y are rotated by an angle ϕ with respect to X_L and Y_L. In the molecular coordinate system, the dielectric tensor ϵ of a locally correlated group of molecules is diagonal with components ϵ_{xx}, ϵ_{yy}, and ϵ_{zz}. By transforming ϵ into the laboratory coordinate system and averaging it over the distribution of ϕ, we obtain the refractive indices

$$n_{X_L}^2 \approx \epsilon_{xx}\langle\cos^2\phi\rangle + \epsilon_{yy}\langle\sin^2\phi\rangle$$

$$n_{Y_L}^2 \approx \epsilon_{xx}\langle\sin^2\phi\rangle + \epsilon_{yy}\langle\cos^2\phi\rangle \qquad (2)$$

$$n_{Z_L}^2 \approx \epsilon_{zz}.$$

From Eqs. (2), the birefringence, $\Delta n = n_{Z_L} - n_{X_L}$, and its variation with field, $\delta\Delta n(E) \approx n_{X_L}(0) - n_{X_L}(E)$, can be calculated for comparison with experiment. For zero field, where the molecules rotate freely, $\langle\cos^2\phi\rangle = \langle\sin^2\phi\rangle = \frac{1}{2}$, and the liquid crystal is optically uniaxial with $n_{X_L}^2 = n_{Y_L}^2 = (\epsilon_{xx} + \epsilon_{yy})/2$. When $E \neq 0$ and the molecular rotation is hindered, these expectation values are not equal and the system becomes biaxial. In the high-field limit, $n_{X_L}^2 \approx \epsilon_{xx}$.

To calculate the expectation values in Eqs. (2), we average over ϕ, employing the mean-field distribution function $\rho(\phi) = \exp(EP_0 \cos\phi/k_BT)$, where P_0 is the transverse component of the electric dipole moment of a locally correlated group of molecules. Noting that $\epsilon_{yy} - \epsilon_{xx} < \epsilon_{xx}$ at optical frequencies, we obtain an approximate expression for the field-dependent change in birefringence $\delta\Delta n$,

$$\delta\Delta n(E) \approx \frac{1}{2}(\epsilon_{yy}^{1/2} - \epsilon_{xx}^{1/2})\frac{I_2(EP_0/k_BT)}{I_0(EP_0/k_BT)}, \qquad (3)$$

where I_0 and I_2 are the modified Bessel functions. The solid curve in Fig. 3(b) is a fit of Eq. (3) to the experimental $\delta\Delta n(E)$, employing $\epsilon_{yy}^{1/2} - \epsilon_{xx}^{1/2} = 0.01$ and $P_0 = 1800$ D. Note that the calculated curve scales as E^2 for small E, then passes through an inflection point and saturates for large E,

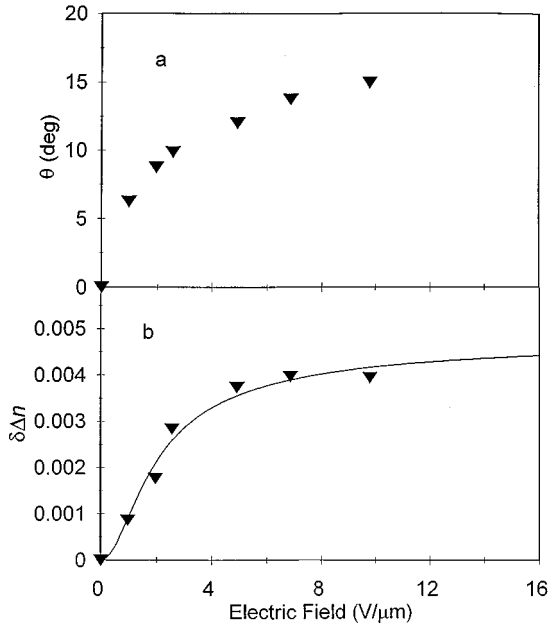

FIG. 3. Variation of (a) the optical tilt angle θ and (b) the change in birefringence $\delta\Delta n$ as a function of applied electric field in the smectic-A^* phase of a 10-μm-thick KN125 liquid crystalline sample; the curve in (b) is a fit of Eq. (3) to the experimental data.

in qualitative agreement with the experimental results. Because the transverse molecular dipole moment for KN125 is approximately 5 D [14], this simple model suggests that each locally correlated group consists of several hundred molecules. A more accurate treatment of this problem should probably account for possible variations of the dipole correlation length with electric field.

Using the fact that $n_{Z_L} \gg \Delta n \gg (n_{Y_L} - n_{X_L})$, one can obtain from Eq. (2) an approximate relation between the field-induced biaxiality $\delta n \equiv n_{Y_L} - n_{X_L}$ and the change in birefringence

$$\delta n(E) \approx 2\,\delta\Delta n(E). \qquad (4)$$

As a result, $\delta n(E)$ may be evaluated directly from the measured $\delta\Delta n(E)$. An alternative way to characterize the induced biaxiality is by the biaxial angle β that the two optical axes for wave normals make with the Z_L axis. β is related to the refractive indices by the expression [11]

$$\tan\beta = \left(\frac{n_{X_L}^{-2} - n_{Y_L}^{-2}}{n_{Y_L}^{-2} - n_{Z_L}^{-2}}\right)^{1/2}. \qquad (5)$$

Combining Eqs. (4) and (5), we obtain the approximate relation $\beta \approx \sqrt{2\,\delta\Delta n/\Delta n}$, indicating that β can be derived directly from the measured values of Δn and $\delta\Delta n(E)$.

In Fig. 4, β is plotted as a function of the tilt angle θ for KN125. The solid curve is a least-square fit of the data, showing that β varies linearly with tilt angle θ over a wide range of electric-field strengths. This also implies that the biaxiality δn is proportional to θ^2 (since δn varies roughly as β^2). A similar correlation between refractive index biaxiality and the smectic-C phase tilt angle has been reported by

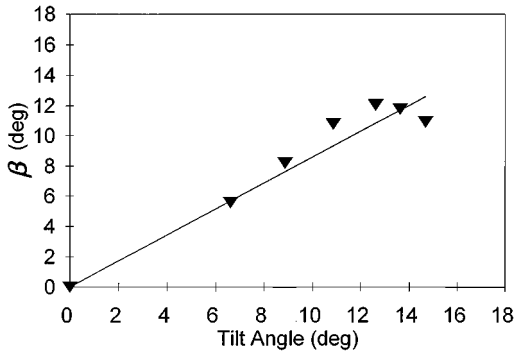

FIG. 4. β, the half angle between the two optic axes, as a function of optical tilt angle for the smectic-A^* phase of KN125. The sample is the same as for Fig. 3. The curve is a linear least-squares fit to the data.

Galerne [15]. The biaxiality measured here for KN125 in the chiral smectic-A^* phase is appreciably larger than that reported earlier for similar tilt angles in the smectic-C phase [15,16]. Gouda *et al.* [1] studied the dielectric biaxiality in a chiral smectic-C^* liquid crystal and also found it to vary as the square of the tilt angle, consistent with our findings. A quadratic dependence of δn on θ is also expected from symmetry arguments. Since the refractive index is a continuous even function of θ, $\Delta n(\theta)=\Delta n(-\theta)$ and $\delta\Delta n \propto \theta^2$. While these arguments establish a clear relationship between θ and δn in the low field limit, the relationship between these two quantities is more general and should hold for a wide range of fields. This is so because the electroclinic tilt as well as the field-induced biaxiality arise due to the force exerted by the field on the dipole moment **P**.

Finally, it should be emphasized that the primary effect caused by the electric field acting on Sm-A^* liquid crystals is the reduction of the azimuthal angle degeneracy. This induces tilt as well as biaxiality, removing two important characteristics that differentiate the Sm-A^* and Sm-C^* phases. The induced optical biaxiality observed here for the chiral smectic-A phase is surprisingly large, particularly when compared to the biaxiality in the smectic-C phase with comparable tilt angles. Our data also show a strong correlation between the electroclinic tilt angle and biaxiality. These results raise fundamental questions regarding the nature of the Sm-A^* phase in the presence of an electric field, and whether a single order parameter and its associated angular distribution might be sufficient to describe the physical properties of Sm-A^*. While further studies are needed to resolve these questions, the optical techniques employed in this work provide a powerful probe of these phenomena.

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