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Investigation of the indices of refraction near the smectic-A–smectic-C transition: Orientational order

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The results of direct measurements of the principal indices of refraction in the smectic-A and smectic-C phases of two homologous liquid crystals are reported. These results are compared qualitatively with the orientational model of Straley and with a model based on anisotropic nematic fluctuations due to coupling between orientational and translational order.

I. INTRODUCTION

The presence of optical biaxiality in the smectic-C phase has been known for several years, but the relationship of this biaxiality to the orientational ordering of the phase is not well understood. For example, one does not yet know the role played by the rotation of the anisotropic molecules about their long axes. A model proposed by McMillan assumes the biaxiality of the phase is due to the partial freeze-out of this rotation, while other models assume this rotation to be essentially free. The experimental literature is somewhat more decisive, but still inconclusive. Some experiments have been interpreted to indicate a very small amount of rotational freeze-out, in agreement with optical experiments in which the biaxiality is found to be small enough to case doubt on the importance of rotational freezeout. In this paper, the results of direct measurements of the principal indices of refraction in the smectic-A and smectic-C phases are presented and the results are compared with two models: (i) the orientational model of Straley and (ii) a model for the orientational order based on the anisotropy of nematic (long-axis) fluctuations as a result of coupling to layer dilation.

II. EXPERIMENTAL

The liquid crystals used are thio-substituted esters, 4-phenylthio-4'-n-octyloxybenzoate (85S) which has been used in other studies and 4-phenylthio-4'-n-nonyloxybenzoate (95S). Both exhibit a nematic–smectic-A transition (at 355.6 K for 85S and at 345.6 K for 95S) and a smectic-A–smectic-C transition (at 329.6 K for 85S and at 335.5 K for 95S).

A Bausch and Lomb 3L Abbe refractometer is used in the transmission mode to measure the refractive indices of planar samples as a function of temperature. The refractometer prisms are prepared for sample alignment by applying and heat-treating a thin coating of polyvinyl alcohol. The prisms are then unidirectionally rubbed antiparallel to each other. The rubbing orientation in a particular experiment is either parallel or perpendicular to the plane defined by the light path through the instrument. In the nematic and smectic-A phases, this treatment aligns the director along the rubbing axis. The smectic-A layers form perpendicular to the prism faces [see Fig. 1(a)]. On cooling into the smectic-C phase, we find that the director remains aligned along the rubbing axis, implying that the layers have tilted with respect to a prism face [see Figs. 1(b) and 1(c)]. The same result was found in another recent experiment using oblique SiO evaporation to align the director. During the course of our experiment, the director alignment relative to the layer normal is verified as follows.

Nematic liquid crystal is applied to completely fill the volume between the prism faces, with a small amount extending beyond the prism edges to reduce wetting effects. The sample is cooled into the smectic-A phase where the director alignment is checked by rotating a polaroid over the eyepiece.

FIG. 1. Domain structures in homogeneously aligned smectic samples and the laboratory coordinate system. (a) Smectic-A phase. (b)–(d) Possible smectic-C configurations as discussed in the text. In each case, the rubbing direction defines the z direction, in (a)–(c) the director is along the z direction, while (d) shows a tilted director. The tilt plane in (b) is the x–z plane and in (c) is the y–z plane.
of the refractometer. A well-aligned sample gives a single distinct polarization-independent reflection borderline for the parallel rubbing orientation. This corresponds to the ordinary refractive index \( n_o \). The perpendicular rubbing alignment shows only two distinct borderlines, one for horizontal polarization, corresponding to the extraordinary index \( n_e \), and one for vertical polarization corresponding again to \( n_o \). In order to check the assertion that indistinct borderlines imply misalignment, samples were prepared in which the director was varied randomly through the sample. These indeed showed indistinct borderlines due to the spatial modulation of the director and hence the index of refraction of the sample. Therefore, any sample not showing distinct reflection borderlines was assumed to have a poorly aligned director and was discarded.

As a further experimental check, the smectic-A indices \( n_e \) and \( n_o \) of homeotropic samples, in which the layers are parallel to the prism faces, were compared with our measurements on homogeneous samples. These results were nearly identical and are shown in Fig. 2.

Upon cooling the liquid crystal into the smectic-C phase, a well-aligned sample gives two distinct borderlines for both rubbing orientations, one for horizontal polarization and one for vertical polarization. To describe these results, it is useful to define a laboratory coordinate system \((x, y, z)\) with the \( z \) axis defined by the rubbing direction and the \( x \) axis defined by the vertical polarization direction. The \( y \) axis is chosen to complete a right-handed system and corresponds to the horizontal polarization direction in the samples with the parallel rubbing orientation. Then \( n_e \), \( n_o \), and \( n_p \) are the refractive indices for waves polarized in the \( x \), \( y \), and \( z \) directions respectively. This coordinate system is shown in Fig. 1. With respect to this coordinate system, we measure \( n_p \) (vertical polarization) and \( n_e \) (horizontal polarization) for parallel rubbing, while for perpendicular rubbing we measure \( n_p \) (vertical polarization) and \( n_e \) (horizontal polarization). In the uniaxial smectic \( A \)-phase, \( n_e \) and \( n_p \) become degenerate and reduce to \( n_o \) whereas \( n_e \) becomes \( n_p \).

The antiparallel rubbing of the two prisms appears to be essential to achieve well-aligned samples in the smectic-\( C \) phase, as evidenced by more distinct borderlines. If the prisms are rubbed parallel to each order, the reflection borderlines become very distinct. This may be due to the competition between the types of domains shown in Figs. 1(c) and 1(b), both of which were found in Ref. 21. Two facts allow us to identify the actual structure of our smectic-\( C \) samples as being only that shown in Fig. 1(b) when the prisms are rubbed antiparallel. First, it is shown that the tilt of the molecules relative to the layer normal occurs in the plane containing the largest and smallest principal axes of the index ellipsoid. Second, the refractive index for vertical polarization \( n_p \) is always smaller than the horizontal polarization indices \( n_e \) and \( n_p \). Thus the structure must be that shown in Fig. 1(b), rather than Fig. 1(c) since the tilt plane must correspond to the \( x-z \) rather than the \( y-z \) plane. If the director did not remain parallel to the prism faces but

![Fig. 2. Principal indices of refraction of S55 in the smectic-A and smectic-C phases. \( n_o, n_e, \) and \( n_p \) should be read using the left-hand scale, while \( n_p \) and \( n_p \) should be read using the contracted scale on the right-hand side. (x) and (y) are data from Ref. 22. (O) are data collected during the present experiment. The slight deviation of the (x) data from the (O) data in the smectic-A phase is probably due to a slightly misaligned homeotropic sample. The nematic data agree well.](image)
tilted as shown in Fig. 1(d), the refractive index \( n_x \) would eventually exceed \( n_y \) as the tilt increased upon continued cooling of the sample. An inspection of the data presented in Fig. 2 shows that \( n_x \) decreases with respect to \( n_y \) below the smectic-A–smectic-C transition temperature, consistent only with the structure shown in Fig. 1(b). In all probability, the antiparallel rubbing induces a small tilt at the surface which is sufficient to bias the tilt orientation of the Smectic-C layers but is too small to produce an observable difference between the \( n_y \) and \( n_x \) values measured in homogeneous as opposed to homeotropic samples. Therefore, the laboratory coordinate system defined above is an appropriate principal-axis system for index-of-refraction measurements.

The results from seven different 8S5 samples and the data of Ref. 22 are shown in Figs. 2 and 3. The scatter of the data is independent of the sample used. Figure 4 shows the result for 8S5.

![Graph](image)

**FIG. 3.** An expansion of the smectic-A–smectic-C transition using only the new data. The lines shown are linear least-squares fits. The slopes of the \( n_x \), \( n_y \), and \( n_z \) lines are \(-6.9 \times 10^{-4}\), \(-8.58 \times 10^{-4}\), \(-2.07 \times 10^{-4}\), and \(2.0 \times 10^{-4}\), respectively.

**FIG. 4.** Principal indices of refraction of 8S5. \( n_x, n_y \), and \( n_z \) (·) should be read using the left-hand scale, while \( n_y \) and \( n_z \) ([·]) should be read using the contracted scale on the right-hand side. All of this data are from homogeneously aligned planar samples. The lines shown are linear least-squares fits. The slopes of the \( n_x \), \( n_y \), \( n_o \), and \( n_z \) lines are \(-9.64 \times 10^{-4}\), \(-7.13 \times 10^{-4}\), \(-1.94 \times 10^{-4}\), and \(-2.05 \times 10^{-4}\), respectively.
III. RESULTS AND DISCUSSION

The most striking feature of the data is that \( n_y \) is a linear continuation of \( n_0 \) in both \( \delta S5 \) and \( \delta S5 \). Linear least-squares fits to the \( n_0 \) data and the \( n_y \) data are shown in both Figs. 3 and 4. The slopes of the lines differ by roughly 4% and 5%, respectively, but the two lines are the same within experimental uncertainty. We note that the data given in Figs. 3 and 4 contrast strongly with the behavior observed by Galerne\textsuperscript{23} in a material which has isotropic–smectic-A and smectic-A–smectic-C transitions. Thus the observed continuity of \( n_0 \) and \( n_y \) for \( \delta S5 \) and \( \delta S5 \) is not a universal feature for all compounds. Possible reasons for the different types of behavior are elucidated when models for the orientational order parameters are examined.

We have analyzed our results under the assumption that the relationship between the indices of refractions, \( n_x \), \( n_y \), \( n_z \) and the thermally averaged molecular polarizabilities \( \alpha_x, \alpha_y, \alpha_z \), in liquid crystals may be adequately approximated by the Lorentz–Lorenz relations\textsuperscript{15}:

\[
\begin{align}
\frac{1}{n_x^2} & = \frac{1}{n_0^2} - \frac{1}{n^2} + \frac{1}{n^2_0} - \frac{1}{n^2} + \frac{1}{n^2_0} - \frac{1}{n^2} \\
\frac{1}{n_y^2} & = \frac{1}{n_0^2} - \frac{1}{n^2} + \frac{1}{n^2_0} - \frac{1}{n^2} + \frac{1}{n^2_0} - \frac{1}{n^2} \\
\alpha_x + \alpha_y + \alpha_z & = \alpha_1 + \alpha_2 + \alpha_3.
\end{align}
\]

Therefore,

\[
\frac{3}{4\pi N} \sum_{i=x,y,z} \frac{n_i^2 - 1}{n_i^2 + 2} = \sum_{i=1}^3 \alpha_i.
\]

(1e)

\( N \) is the molecular number density and \( \alpha_{x,y,z} \) are components of the diagonalized molecular polarizability tensor. From Eq. (1e) we see that the temperature dependence of \( N \) must be the same as that of

\[
\sum_{i=x,y,z} \frac{n_i^2 - 1}{n_i^2 + 2},
\]

which allows us to test the validity of Eq. (1a)–(1e). Our auxiliary measurements of \( N \) as a function of temperature reveal that the left-hand side of Eq. (1e) has some temperature dependence suggesting that local-field effects that are left out of the Lorentz–Lorenz approximation are in fact required to form a complete description of our results. We show, however, such corrections are not required to explain the most striking feature of the data, namely the continuity of \( n_y \) and \( n_z \) through the smectic-A–smectic-C transition.

Thus the direct interpretation of the continuity of \( n_0 \) and \( n_y \) is that the average molecular polarizability in the \( y \) direction (i.e., perpendicular to the tilt plane) is unaffected by the smectic-A–

smectic-C phase transition.

A useful mathematical formalism for the treatment of orientational order in optically uniaxial and biaxial phases is the model proposed by Straley. Although it was originally developed to describe phases without spatial (smectic) order, the fact that the changes in the indices of refraction at the nematic–smectic-A transition are often very small suggests that the effects of coupling between spatial and orientational order can sometimes be neglected as a first approximation. A theory that explicitly couples orientational and spatial order for the smectic-C phase would be desirable, though at present we know of none.

Straley's model expresses the orientational order in terms of thermal averages of functions of the three Euler angles \((\alpha, \beta, \gamma)\) needed to rotate the laboratory frame into a molecular tensor frame. The angles are those defined by Rose.\textsuperscript{24} The molecular axes are chosen such that the molecular polarizability tensor is diagonal and is of the form

\[
\alpha_{\alpha} = \begin{pmatrix}
\alpha_1 & 0 & 0 \\
0 & \alpha_2 & 0 \\
0 & 0 & \alpha_3
\end{pmatrix},
\]

where \( \alpha_1 < \alpha_2 < \alpha_3 \) are the principal molecular polarizabilities. The molecular \( x, y, \) and \( z \) axes correspond to \( \alpha_1, \alpha_2, \) and \( \alpha_3, \) respectively. The average polarizability tensor in the laboratory frame is given by

\[
\overline{\alpha} = \mathcal{R}(\alpha, \beta, \gamma) \alpha \mathcal{R}(\alpha, \beta, \gamma)^T,
\]

(3)

where angular brackets mean a thermal average. The elements of \( \overline{\alpha} \) must be unchanged under the set of Euler-angle transformations which leaves both the phase and the molecular tensor invariant. Since \( \alpha_{\alpha} \) in general has the symmetry of the biaxial index ellipsoid (i.e., three twofold axes of rotation) our choice of \( \alpha_{\alpha} \) as being diagonal is justified. This constraints with the recent analysis of magnetic resonance experiments\textsuperscript{8,9,17} for which the molecular tensor has lower symmetry, and diagonalization is not helpful.

In accordance with Straley, who considered rectangular, block-shaped molecules, the three twofold axes of the molecular polarizability lead to a description of the average polarizability in the laboratory frame in terms of the following four order parameters:

\[
\begin{align}
S &= \frac{1}{2} \cos^2 \beta - \frac{1}{2}, \\
U &= \sin \beta \cos 2\beta, \\
T &= \sin^2 \beta \cos 2\alpha, \\
V &= \frac{1}{2} \left( 1 + \cos^2 \beta \right) \cos 2\alpha \cos 2\gamma - \cos \beta \sin 2\alpha \sin 2\gamma.
\end{align}
\]

(4)
The laboratory frame polarizabilities are then
\[ \alpha_x = \alpha_y = \alpha_z + \frac{1}{2} U(a_2 - a_1) - \frac{1}{2}(S - 1)(\alpha_z - \alpha_x) \]
\[ - \frac{1}{2} T(a_3 - \alpha_y) - \frac{1}{2} V(a_2 - \alpha_z), \]
\[ \alpha_x = \alpha_y = \alpha_z + \frac{1}{2} U(a_2 - a_1) - \frac{1}{2}(S - 1)(\alpha_z - \alpha_x) \]
\[ + \frac{1}{2} T(a_3 - \alpha_y) + \frac{1}{2} V(a_2 - \alpha_z), \]
\[ \alpha_x = \alpha_y = \alpha_z + \frac{1}{2} U(a_2 - a_1) + \frac{1}{2}(S - 1)(\alpha_z - \alpha_x), \]
where \( \alpha_x = \frac{1}{2}(\alpha_x + \alpha_y). \)

The off-diagonal elements of \( \alpha_{ij} \) are zero. The description of the orientational order of the molecules as reflected in the optical properties is thus contained in the four order parameters \( S, T, U, \) and \( V \) which are interrelated yet nonetheless reveal distinctive information. The parameter \( S \) depends only on the thermal distribution of the angle between the molecular axis of largest polarizability (conventionally called the long axis) and the laboratory director \( \hat{n} \). If the molecules are all aligned with their long axes parallel to the director, then \( S \) is one, so that the quantity \( 1-S \) essentially measures the deviations of the long axes from perfect alignment with the director. Like \( S \), the parameter \( U \) is also uniaxial since it requires for its definition only the existence of the single laboratory axis \( \hat{n} \). It compares the fluctuations for which the director lies in the 1-3 molecular polarizability plane with those for which the director lies in the 2-3 molecular plane. This parameter will be zero if the molecule is rotating freely about its long axis, or if the long axes are all perfectly aligned with the director. In contrast the parameter \( T \) measures the anisotropy of the fluctuations of the molecular long axes in the laboratory frame. It will be nonzero only in a biaxial phase. Finally we note that \( V \) is more complicated and depends on all three Euler angles. Because \( V \) is zero if the molecules rotate freely on their long axes or if the phase is uniaxial it is useful to think of it as a coupling between the order described by \( U \) and \( T \). If the long axes are perfectly aligned \( V \) becomes \( \cos(2(\alpha + \gamma)) \) where the Euler angles \( \alpha \) and \( \gamma \) are not unique but the sum \( \alpha + \gamma \) is well defined for a given molecular orientation. As the temperature goes to zero and the molecules become perfectly ordered orientationally, \( S \) and \( V \) go to one and \( U \) and \( T \) go to zero.

In Straley's model the transition temperatures between isotropic, uniaxial and biaxial phases are obtained for a range of width, breadth, and length values for the molecules. It was found that at the special point \( W = 1, B = 10^{1/2}, \) and \( L = 10 \) a second-order isotropic to biaxial transition with \( S, T, U, \) and \( V \) all growing smoothly from zero occurred. For other values of \( B \) a first-order isotropic-uniaxial transition was followed at lower temperature by a second-order uniaxial-biaxial transition. In the uniaxial phase \( S \) was large and \( U \) small while in the biaxial phase \( V \) predominated over \( T \). Of particular relevance is the fact that compared to a continuation of the uniaxial temperature dependence, \( U \) decreases and \( S \) increases in the biaxial phase.

We now describe the data shown in Figs. 3 and 4 in terms of the four order parameters and the qualitative application of the Lorentz-Lorenz relation. In the smectic-A phase we have
\[ \alpha_x^4 = \alpha_y^4 = \alpha_z^4 + \frac{1}{2} U_A(a_2 - a_1) - \frac{1}{2}(S_A - 1)(\alpha_z - \alpha_x) \]
and
\[ \alpha_x^4 = \alpha_y^4 = \alpha_z^4 + \frac{1}{2} U_A(a_2 - a_1) + \frac{1}{2}(S_A - 1)(\alpha_z - \alpha_x). \]

Subtracting the smectic \( A \) expressions from the corresponding formulae for the \( C \) phase and defining \( \Delta U = U_C - U_A \) and \( \Delta S = S_C - S_A \), we obtain
\[ \alpha_x^C - \alpha_y^C = (a_2 - a_1)(\frac{1}{2} \Delta U - \frac{1}{2} T) + (a_2 - a_1)(-\frac{1}{2} \Delta S - \frac{1}{2} T), \]
\[ \alpha_y^C - \alpha_z^C = (a_2 - a_1)(\frac{1}{2} \Delta U + \frac{1}{2} T) + (a_2 - a_1)(-\frac{1}{2} \Delta S + \frac{1}{2} T), \]
\[ \alpha_z^C - \alpha_x^C = (a_2 - a_1)(-\frac{1}{2} \Delta U) + (a_2 - a_1)(\frac{1}{2} \Delta S). \]

The temperature dependence of the polarizabilities in the smectic \( A \) relates the quantities \( U_A \) and \( S_A \) with the particle density and the respective refractive indices. However, in the \( C \) phase the deviation of \( \alpha_x^C \) from the \( A \)-phase temperature dependence is weakened by the cancellation of \( \Delta U \) with \( V \) and of \( T \) with \( \Delta S \). This cancellation is likely because \( \Delta U < 0, \Delta S > 0, T > 0, \) \( V > 0 \) are expected. For \( \alpha_x^C \) the deviation is enhanced due to the adding together of these terms rather than cancellation. Therefore, qualitatively the Straley model describes the data. Quantitatively, a range of different temperature dependences will occur corresponding to different values of \( a_2 - a_1 \) and \( a_3 - a_1 \), which appear explicitly and are implicitly related to the \( W, B, L \) values which parametrize the model. Whether or not such a cancellation must be fortuitous awaits specific interaction-model calculations.

An alternative model which also qualitatively describes the data consists of ignoring the biaxiality of the molecular polarizability and any attendant rotational freeze-out. The polarizabilities then become
\[ \alpha_x^C = (a_2 - a_1)[-\frac{1}{2}(S - 1) - \frac{1}{2} T], \]
\[ \alpha_y^C = (a_3 - a_1)[-\frac{1}{2}(S_z - 1) + \frac{1}{2} T], \]
\[ \alpha_x^C = (a_3 - a_1)[\frac{1}{2}(S - 1)]. \]

The quantities
\[ - \frac{1}{8}(S - 1) + \frac{1}{2} T = \langle \sin^2 \beta \sin^2 \alpha \rangle \]
and
\[-\frac{1}{2}(S-1) + \frac{1}{2}T] = \langle \sin^2 \beta \cos^2 \alpha \rangle,
\]
so it is clear that \( \alpha \) and \( \beta \) will differ when there is anisotropy in the fluctuations of the long molecular axes.

Going beyond the formalism and introducing coupling to spatial order, the fluctuations in the \( x-z \) plane (\( \alpha = 0 \)) couple in first order to layer dilations and are therefore of high energy and low probability. Conversely, fluctuations in the \( y-z \) plane couple only in second order to layer dilation as do all polar-angle fluctuations in the smectic-\( A' \) phase and are thus of lower energy and higher probability. Hence it might be expected that \( \alpha \) would remain essentially continuous at the transition since \( \alpha = \frac{1}{2} \pi \) fluctuations couple to layer dilations in the same order as the smectic-\( A' \) phase (second order) whereas \( \alpha \) would be expected to decrease below the smectic-\( A' \)–smectic-\( C \) transition because \( \alpha = 0 \) fluctuations couple to layer dilations in first order. This is what is found experimentally and certainly this explanation is the most straightforward, depending only on the symmetry of the phase.

As a final point we note that \( n_\beta = n_\alpha \) for either \( \delta S \delta \) or \( \delta S \) but in fact increases more rapidly with decreasing temperature consistent with the fact that \( \sigma_0 = \frac{1}{2}(n_\beta + n_\alpha) < n_\alpha \). Specifically, we find that
\[
\frac{dn_\beta}{dT} = 1.24 \frac{dn_\alpha}{dT}
\]
for \( \delta S \delta \) and 1.35 \( \frac{dn_\alpha}{dT} \) for \( \delta S \).

In summary we have presented measurements for each of the principal indices of refraction for the two liquid-crystalline compounds \( \delta S \delta \) and \( \delta S \) in the smectic-\( A \) and smectic-\( C \) phases. The fact that the refractive index for light polarized perpendicular to the smectic-\( C \) tilt plane is unaffected by the smectic-\( A' \)–smectic-\( C \) transition is the predominant feature. Qualitatively both the orientational model of Straley and a simpler model neglecting the molecular biaxiality can account for the observations. For quantitative comparison it is desirable for theoretical calculations to be done for Straley’s model and for an extended model including spatial smectic order. To further clarify the situation experimentally, it would be useful to study an appropriate homologous series of compounds to observe whether crossover occurs to the type of behavior observed by Galerne when the smectic-\( A' \)–smectic-\( C \) transition comes progressively closer to the clearing point or, more specifically, when the nematic order parameter at the smectic-\( A' \)–smectic-\( C \) transition becomes progressively smaller.

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