Chirality, surface anchoring, and the cholesteric-smectic A phase transition

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Chirality, surface anchoring, and the cholesteric–smectic A phase transition

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Magnetic Freedericksz transition measurements were performed on samples of chiral and racemic mixtures in the cholesteric/nematic phase. We found that the quantity Φ, which is defined as the threshold field H_{th} times the cell thickness, is larger for the chiral than for the racemic mixtures. This result is inconsistent with chiral contributions to the anchoring strength potential. Instead, the data support a model by Lubensky wherein the transition temperature to the smectic A phase is suppressed in a chiral liquid crystal.

1. Introduction

Chirality and symmetry have long played important roles in liquid crystal physics. In 1975 Meyer et al., 'invented' ferroelectric liquid crystals by means of symmetry arguments applied to a chiral smectic C phase [1]. These materials have since garnered enormous attention in both the fundamental and device oriented communities [2]. More recently, Renn and Lubensky predicted the existence of a periodic array of screw dislocations in a smectic A phase consisting of chiral molecules [3]. Just below the cholesteric–smectic A (Ch–S_A) phase transition, where the penetration depth λ of dislocations is large, this 'twisted grain boundary' smectic A* phase may be more stable than either the untwisted smectic A or the cholesteric phase. Experiments have since confirmed the existence of the smectic A* phase [4, 5]. Along other lines, it has long been known that at an interface, where translational symmetry is broken, a component of polarization exists normal to the interface; this phenomenon was first observed experimentally in the smectic O phase [6]. For a *chiral* nematic tilted by an angle θ with respect to the interface, no local symmetry exists; in consequence the polarization at the interface can have an arbitrary orientation, including a non-zero transverse component perpendicular to the molecule and parallel to the interface. This behaviour was recently demonstrated in several electro-optical experiments [7, 8], raising the

question of whether this additional polarization component P_t contributes to the anchoring strength coefficient W.

In 1975 Lubensky suggested that the Ch–S_A transition should be first order [9], in analogy with type I superconductors in an external magnetic field. Additionally, he pointed out that the transition temperature T_{Ch-S_A} will be shifted downward from the analogous nematic–smectic A transition temperature T_{N-S_A} for the racemic mixture. Based on dimensional and scaling arguments, Lubensky estimated that this temperature shift $\Delta T[= T_{N-S_A} - T_{Ch-S_A}]$ would be a few hundreds of mK for materials with transition temperatures of order 300 K. Developed well before the smectic A* model, the prediction of the phase transition temperature suppression remains essentially valid as long as the penetration depth λ is small. However λ can become large near T_{Ch-S_A}, resulting in the appearance of a smectic A* phase between the cholesteric and the helix-free smectic A phases. Yet, even if a smectic A* phase appears, it may be stable only in a very narrow temperature region, thus preserving the essence of Lubensky's prediction for ΔT [9].

In this paper we report on magnetic Freedericksz transition measurements in the homeotropic (bend) geometry which were designed to elucidate several features of the Ch–S_A phase transition. We examine the effects of chirality on the anchoring strength coefficient W, where the interfacial free energy has a term of the Rapini–Papoular form $F_i = \frac{1}{2} W \theta^2$ [10]. Since the transverse component of polarization P_t is proportional to θ [7, 8], and there exists a term $\propto P_t^2$ in the interfacial free energy, in principle W contains a term due to the chiral

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nature of the molecules. Additionally, we examine the effects of chirality on the Ch–S$_A$ phase transition temperature in light of the Lubensky model. By measuring the Freedericksz threshold field H_{th} for both chiral and racemic materials in wide ($t \simeq 51 \, \mu m$) and narrow ($t = 6 \, \mu m$) sample cells, we have been able to draw the following conclusions: First, the effect of chirality on the anchoring strength coefficient is sufficiently small so that it cannot be extracted from other, more significant, factors influencing H_{th}. Second, we have inferred a depression in T_{Ch-S_A}, relative to T_{N-S_A}, of the order 1 K, consistent with Lubensky's predictions and measurements by Collings [11]. Finally, for both chiral and racemic materials, we have found an apparently negative anchoring strength coefficient. This behaviour can be explained in terms of the ion adsorption model of Barbero and Durand [12–14].

In their seminal work on the electroclinic effect above the smectic A–smectic C* phase transition temperature, Garoff and Meyer [15, 16] wrote down a Landau free energy expansion $F = F_A + \frac{1}{2}A'(T)\theta^2 + \frac{1}{2}\chi_P^{-1}P_t^2 - P_t E - 8\pi^{-1}\varepsilon^0 E^2 - \tau\theta P_t$, where P_t is the transverse polarization, E an electric field applied in the plane of the smectic layers, ε^0 the dielectric constant in the absence of a permanent dipole, χ_P the generalized susceptibility, and τ the coefficient coupling θ and P_t. Additionally, $A'(T) = A(T) + \chi_P\tau^2$, where $A(T)$ is the (non-chiral) inverse tilt susceptibility, which vanishes at the smectic A–smectic C phase transition. If we adopt a two-dimensional analogue of this expression to describe a homeotropically-aligned interface, we find in the absence of an external electric field that $F = F_A + \frac{1}{2}W_0\theta^2 + \frac{1}{2}\chi_P^{-1}P_t^2 - \tau\theta P_t$, where W_0 is the anchoring strength coefficient for a racemic material. Minimizing F with respect to P_t, we find that $F = F_A + \frac{1}{2}W\theta^2$, where the effective anchoring strength coefficient $W = W_0 - \chi_P\tau^2$. Thus, for chiral materials, one expects a reduction of the effective anchoring strength coefficient from that of its racemic mixture.

In a magnetic Freedericksz experiment in the bend geometry, the threshold field H_{th} is given implicitly by the equation [10]

$$\cot\left(\frac{\pi}{2}\frac{H_{th}}{U_3}\right) = \frac{\pi K_{33}}{tW}\frac{H_{th}}{U_3}, \qquad (1)$$

where K_{33} is the bend elastic constant and t is the cell thickness. Additionally, U_3 is the Freedericksz threshold field in the limit that W is very large, namely $U_3 = \pi/t\sqrt{(K_{33}/\Delta\chi)}$ where $\Delta\chi$ is the magnetic susceptibility anisotropy. Equation (1) can be made more transparent by expanding H_{th}/U_3 about unity:

$$\Phi \equiv H_{th}t \approx \pi\sqrt{\left(\frac{K_{33}}{\Delta\chi}\right)} - \frac{2\pi K_{33}}{tW}\sqrt{\left(\frac{K_{33}}{\Delta\chi}\right)}. \qquad (2)$$

For cells of a given thickness, the quantity Φ decreases as

the anchoring becomes weaker, and thus a chiral material should exhibit a smaller value of Φ than its racemic counterpart. Physically, this is quite reasonable, as additional avenues for reduction of the free energy in a field are available to the chiral sample. Thus, from equation (1) or (2), one can extract the anchoring strength coefficient W by using the well-established technique for measuring H_{th} for a given species in both wide and narrow cells [17].

Cells were prepared using ordinary microscope slides. The glass was cleaned sequentially in Alconox® soap, distilled water, acetone, and ethanol. The surfaces were then treated with the surfactant hexadecyltrimethylammonium bromide (HTAB) to promote homeotropic alignment. Measurements were also peformed with other surfactants, such as hexadecylamine, with virtually no quantitative difference in the results. Four cells were prepared: two narrow and two wide, such that the empty cell thicknesses were determined by interferometry at approximately 80°C [17]. (By performing the thickness measurements near the temperatures at which the experiment would be performed, difficulties arising from thermal expansion of the glass and epoxy were obviated). The cells were filled in the isotropic phase and then allowed to cool into the cholesteric phase. Data for the four samples are given in the table. The chiral mixture SCE12 and its racemate SCE12R were obtained from E. Merck Ltd., and used without further purification. The two chiral materials W46(r, r) and W46(s, s) were obtained from Displaytech and used without further purification.

Crandall *et al.*, recently demonstrated [18] that the electric Freedericksz transition threshold voltage V_{th} for a chiral, homeotropically aligned, negative dielectric anisotropy material is maximum when the pitch P_0 is infinite, and decreases for finite P_0

$$V_{th} = \frac{\pi^2}{|\Delta\chi|}\left(K_{33} - \frac{4K_{22}^2 t^2}{K_{33}P_0^2}\right). \qquad (3)$$

Data for the four samples used.

Cell	Mixture (per cent)	Thickness/μm
NC (narrow chiral)	40 SCE12 60 W46(r, r)	(6·07 ± 0·05)
NR (narrow racemic)	40 SCE12R 30 W46(r, r) 30 W46(s, s)	(6·51 ± 0·05)
WC (wide chiral)	40 SCE12 60 W46(r, r)	(51·4 ± 0·1)
WR (wide racemic)	40 SCE12R 30 W46(r, r) 30 W46(s, s)	(51·7 ± 0·1)

In fact, for $P_0 < 2tK_{22}/K_{33}$, surface stabilization breaks down: the liquid crystal is no longer a homeotropic monodomain, but rather forms a pattern of localized twisted domains. (Note that equation (3) applies to cells in which the anchoring is strong, i.e. $W \to \infty$.) Thus, to investigate manifestations of P_t on anchoring, it is important to choose a chiral mixture for which the bulk helical pitch is unwound ($P_0 \to \infty$), yet for which a net transverse dipole moment still exists. In this way artifacts arising from (incipient) helicity may be avoided. Thus the so-called 'chiral' mixture was actually composed of two materials with opposite pitch, so that at a particular temperature in the cholesteric phase $P_0 \to \infty$. The 'racemic' mixture consisted of the corresponding mixture of SCE12R (the commercially produced racemic version of SCE12), plus equal components of left-handed and right-handed W46.

A given sample was inserted into an oven thermally stabilized to 10 mK, which was in turn placed in the bore of a superconducting magnet with transverse optical ports; the magnetic field H was oriented parallel to the cell. Light from a 5 mW He–Ne laser passed consecutively through a polarizer, the sample, an analyser, a light chopper, and into a detector. The detector output was input to a lock-in amplifier, referenced to the chopper frequency. The field was ramped upward at a rate of $0{\cdot}65\,\text{G s}^{-1}$ for the wide samples, and at a rate of $9\,\text{G s}^{-1}$ for the narrow samples. A clean Freedericksz transition threshold was observed, and the H_{th} versus temperature data are plotted in figure 1 for the narrow samples and in figure 2 for the wide samples. We note that the transition temperature T_{Ch-S_A} of the chiral samples was found to be $(82{\cdot}3 \pm 0{\cdot}1)°C$, whereas for the racemic samples we found T_{N-S_A} to be $(80{\cdot}6 \pm 0{\cdot}1)°C$, as determined by optical microscopy. This is in contrast to the prediction by Lubensky [9], in which the transition temperature is expected to be reduced for the case of a chiral material. We are not concerned with this disagreement, however, inasmuch as SCE12 and SCE12R each involve about ten components. It is likely that the temperature disparity is due to small concentration differences in our chiral and racemic mixtures. Later we shall look at other evidence which suggests that the materials are behaving as predicted in [9].

In figure 3 we combine the results of figures 1 and 2, plotting the quantity $\Phi[= H_{th}t]$ versus temperature. Since K_{33} has both a regular and a divergent component, we need to examine the anchoring strength coefficient at a temperature where K_{33} is identical for both the chiral and racemate (cf. equations (1) and (2)). Therefore, in figure 3 we have shifted the chiral data downward in temperature by $1{\cdot}7°C$, so that the two transition temperatures coincide. This facilitates comparisons among the samples by comparing their behaviour at temperatures relative to their respective transitions into the smectic A
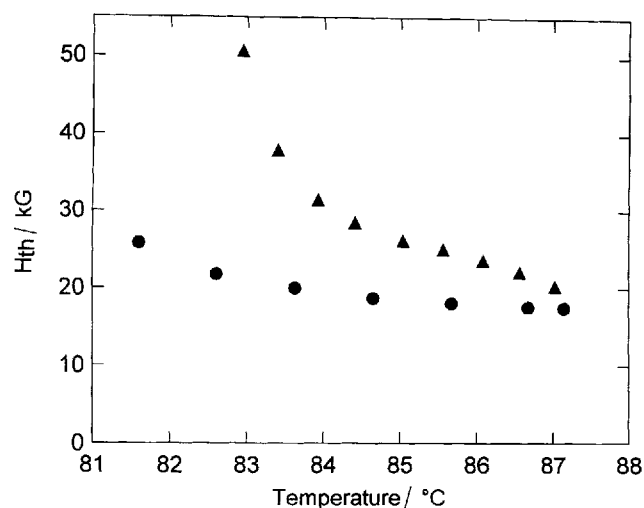

Figure 1.   Freederickz transition threshold H_{th} versus temperature for the narrow samples. The solid triangles correspond to the chiral data (NC) and the solid circles to the racemic data (NR).
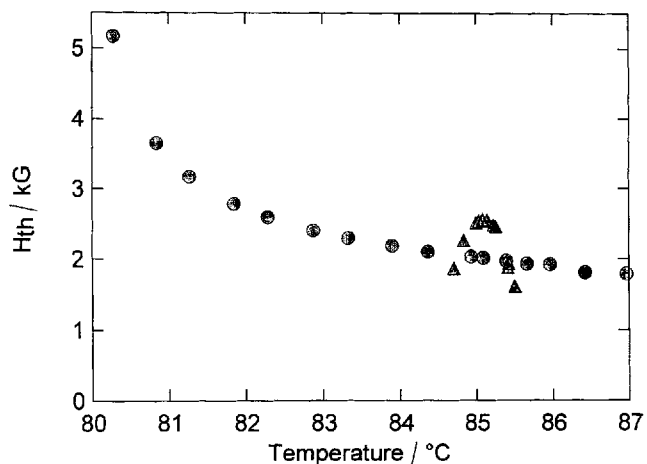

Figure 2.   Freedericksz transition threshold H_{th} versus temperature for the wide samples. The light triangles correspond to the chiral data (WC) and the light circles to the racemic data (WR).

phase. In doing this we have made two assumptions which will be examined later. First, we have assumed that the temperature dependence of the divergent part of K_{33} is identical for both chiral and racemate. Second, we have assumed that the measurements were made sufficiently deeply into the nematic/cholesteric phase that any issues arising from the temperature dependence of the nematic order parameter can be neglected.

From equation (3) and the wide chiral (WC) data in figure 3, it's clear that the pitch diverges at the normalized temperature $T_N = 83{\cdot}1°C$; all comparisons must therefore be made at this temperature. First, comparing the values of Φ for the wide (WR) and narrow (NR) *racemic* samples,
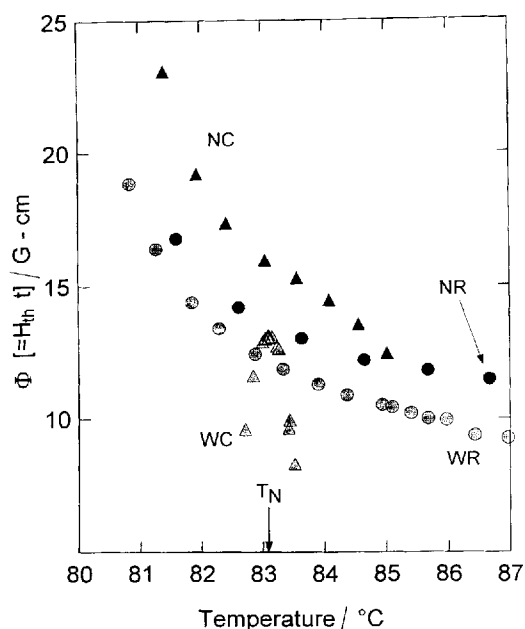
Figure 3. The quantity $\Phi = H_{th} \times$ sample thickness versus temperature. The temperature scale for the chiral data has been shifted down by 1·7°C, so that the transition temperatures overlap. The solid triangles correspond to the narrow chiral (NC), the solid circles to the narrow racemic (NR), the light triangles to the wide chiral (WC), and the light circles to the wide racemic (WR) data. T_N, the temperature at which the chiral pitch unwinds, is shown.

we find a curious result: for the narrow cell Φ is greater than for the wide cell. It is important to remember that we are comparing two sets of data involving the same racemic material, and thus no relative temperature shifts are involved. From equation (2) this behaviour would seemingly indicate a negative anchoring strength coefficient, which is clearly a nonphysical result. Several years ago Barbero and Durand pointed out [12, 13] that impurity ions in the liquid crystal tend to adsorb on the cell surfaces; for thicker cells (i.e. for more liquid crystalline material), the concentration of adsorbed ions is larger. The resulting classical double layer, with a thickness of order the Debye screening length, results in an electric field at and normal to the interface. If the homeotropic liquid crystal has a positive dielectric anisotropy $\Delta\varepsilon$, the resulting field tends to stabilize the alignment, giving rise to stronger anchoring in wide samples (where the adsorbed charge density is larger). On the other hand, if $\Delta\varepsilon < 0$, which is the case for our materials, the field tends to destabilize the homeotropic anchoring. For wider cells, the reduction in the effective anchoring strength coefficient, which involves both the inherent part and this field contribution, is larger than for narrower cells. This effect has been examined experimentally for both planar and homeotropic alignment [14, 19], such that in the planar

configuration destabilization occurs for $\Delta\varepsilon > 0$. Valenti *et al.*, for example, found [14] that the threshold voltage for planar alignment of pentylcyanobiphenyl ($\Delta\varepsilon > 0$) decreases by half when the cell spacing increases from 5 to 60 μm. Our results are apparently consistent with Barbero and Durand's explanation, as adsorbed ions tend to destabilize our wide sample ($\Delta\varepsilon < 0$), giving rise to a decrease in Φ. From figure 3 and equation (2) we see that the value for Φ, which is of order 20 per cent smaller for the wide sample, would imply that

$$2K_{33}\left(\frac{1}{t_w W_w} - \frac{1}{t_n W_n}\right) \approx 0.2,$$

where the subscripts w and n refer to 'wide' and 'narrow', respectively. Taking $K_{33} \sim 10^{-6}$ dyn and assuming that for the narrow cell $W_n = 5 \times 10^{-2}$ erg cm^{-1}, we find that $W_w \approx 1.5 \times 10^{-3}$ erg cm^{-1}. This corresponds to a rather substantial reduction in the anchoring strength due to ionic adsorption—nearly equal to W_n itself—consistent with that found in [14] for planar samples. If we assume instead that $W_n \to \infty$, corresponding to completely rigid anchoring and therefore to the case where $H_{th} \approx U_3$ in the narrow sample, we find that $W_w \approx 2 \times 10^{-3}$ erg cm^{-1}. Qualitatively, we find the same sort of behaviour with the chiral cells at the normalized temperature $T_N = 83·1°C$, where the helical pitch unwinds. The difference in Φ between wide and narrow chiral samples is greater, which may be due to a larger impurity ion concentration in the chiral sample.

In principle, if U_3 could be independently obtained with a sufficient degree of accuracy, it would be possible to separate the desired effects of chirality from the unwanted effects of ion adsorption. Unfortunately this is not possible. For the examples given above, the (negative) contribution to the anchoring strength potential in the wide cells from the surface double layer is only slightly smaller than the (positive) inherent anchoring strength; thus, a small chiral contribution to W from P_t would be difficult to separate out from the adsorbed ion contribution. We can estimate the contribution which might be expected from the transverse dipole moment at the interface. Assuming that the interfacial polarization P_t interacts with a *single* image dipole of comparable magnitude, we obtain an energy per unit area $F_P \sim ((P_t^0 V)^2/\varepsilon r^3 A)\theta^2$, where P_t^0 corresponds to a polarization per radian of tilt, V the volume of the molecule, and A its area. Taking $V \sim 10^{-21}$ cm^3, $A \sim 3 \times 10^{-15}$ cm^2, $\varepsilon \sim 6$ [20], $r \sim 10$ Å, and a value for P_t comparable to that of many chiral smectic C liquid crystals [2], namely $P_t^0 \sim 100$ esu cm^{-2} rad^{-1}, we obtain $F_P \sim (2 \times 10^{-3})\theta^2$ erg cm^{-2}. Although small, this contribution to the anchoring strength coefficient W would likely have been observable in the absence of the ionic term.

It is clear that by comparing the narrow and wide cell data for an individual material in figure 3 that the anchoring is determined principally by the inherent anchoring plus the double layer term; chirality plays at most a small role. Nevertheless, for cells of approximately equal thickness, one would still expect the anchoring strength for the chiral material to be slightly less than that of the racemic material. From equation (2), we would therefore expect the quantity Φ for the chiral liquid crystal to be less that its racemic counterpart. In figure 3 we see, in fact, that the opposite is true: Φ for the chiral is larger—substantially so—than its value in the racemate. (It is important to realize, of course, that chirality may be influencing Φ in the expected manner, such that the chiral threshold fields are indeed suppressed *slightly*, but not sufficiently to overcome other effects such as ion adsorption and those to be discussed below.) The question then arises: Why are the chiral thresholds in the wide and narrow cells *larger* than their racemic values in their corresponding wide and narrow cells? Our simple Landau model, as does any other symmetry-based argument, suggests that chirality *weakens* anchoring. Additionally, if the ionic impurity concentrations of the chiral material were, indeed, larger than the racemate, as discussed in the previous paragraph, we would expect a *suppression* of the chiral threshold, not the experimentally observed enhancement. In this light we need to re-examine our initial assumptions about equating the transition temperatures and the divergent part of K_{33}.

Earlier we had assumed that by shifting the temperature scales so that $T_{\text{Ch-S}_A}$ corresponds to $T_{\text{N-S}_A}$, the bend elastic constants, including their divergent parts, would be equivalent at the same reduced temperature T_N relative to the smectic A transition temperature. A second supposition was that the regular part of K_{33}, which depends upon the nematic order parameter, is identical at $T_N = 83\cdot1°C$, even though the isotropic transition temperatures do not coincide after shifting $T_{\text{Ch-S}_A}$ to match $T_{\text{N-S}_A}$. We feel that the latter is an excellent approximation. Assuming rigid anchoring, from the first term on the right hand side of equation (2) we see that the chiral value of K_{33} would need to be larger than its racemic value by approximately 25 per cent to explain the data. This is a highly unlikely scenario. Since the isotropic transition is at least 20°C above T_N, the nematic order parameter will be near saturation, and both it and K_{33} are very weak functions of temperature near T_N. Instead, we need to reexamine our first assumption, which deals with the divergent part of K_{33} near the smectic A transition.

Although we have compared the chiral and racemic data at a given temperature T_N relative to their respective smectic A transition temperatures, Lubensky's model indicates that this procedure may be inappropriate. In the racemate, K_{33} contains a term which diverges as T

approaches $T_{\text{N-S}_A}$. In the chiral material, however, the situation is more complicated. At the temperature T_N, where the helix unwinds, K_{33} also possesses a regular and a divergent part. We suggest, however, that the latter would diverge *not toward* $T_{\text{Ch-S}_A}$, but rather toward some higher temperature $T_{\text{N-S}_A}^*$. $T_{\text{N-S}_A}^*$ corresponds to the extrapolated *divergence* temperature of K_{33} only when the chiral sample is at its unwinding temperature T_N. The argument is as follows: As the temperature is decreased below T_N, the bulk chiral liquid crystal begins to twist. Thus, for a given temperature T (which corresponds to a particular pitch P_0), according to [9] we can associate a pitch-dependent—and therefore temperature-dependent—*transition* temperature $T_{\text{Ch-S}_A}(T)$; this is to be distinguished from the *divergence* temperature $T_{\text{N-S}_A}^*$ of K_{33} for the unwound chiral sample. Near T_N, where P_0 is large, $T_{\text{Ch-S}_A}$ would be close to $T_{\text{N-S}_A}^*$. At lower temperatures, however, where the pitch is smaller, $T_{\text{Ch-S}_A}$ is reduced and is therefore somewhat below $T_{\text{N-S}_A}^*$. Thus, as we lower the temperature of the chiral nematic, its corresponding transition temperature $T_{\text{Ch-S}_A}(T)$ into the smectic A phase creeps downward. Eventually, we catch up and the sample enters the smectic A phase at $T_{\text{Ch-S}_A}$ ($T = 80\cdot6°C$) = 80·6°C. As suggested by Lubensky [9], this transition temperature $T_{\text{Ch-S}_A}$ is lower than $T_{\text{N-S}_A}^*$ due to chirality. Thus, we should *not* have shifted the chiral temperature scale to equate the actual transition temperature $T_{\text{Ch-S}_A}$ with the racemic $T_{\text{N-S}_A}$, but instead should have equated the extrapolated K_{33} divergence temperature $T_{\text{N-S}_A}^*$ of the unwound chiral material with $T_{\text{N-S}_A}$. Since $T_{\text{N-S}_A}^* > T_{\text{Ch-S}_A}$, we still need to shift the chiral data downward by several hundreds of millikelvins, according to [9]. By shifting the chiral data downward in temperature by approximately 700–900 mK, we find that the value of Φ for the unwound chiral material is equal to its value for the racemate. The same procedure is valid for both the wide and narrow cells. Thus, it appears that the larger Φ associated with the chiral material is due to equating $T_{\text{Ch-S}_A}$, rather than $T_{\text{N-S}_A}^*$, with $T_{\text{N-S}_A}$. Although this does not constitute a conclusive proof of Lubensky's model, it does support his calculation that the transition temperature to the smectic A phase is suppressed in a chiral material.

A similar chiral-induced reduction of $T_{\text{Ch-S}_A}$ has also been observed by Collings [11]. Using chiral thioester mixtures with chiral fraction ranging from 0 (racemic) to 1 (pure enantiomer), he found that $T_{\text{Ch-S}_A}$ decreases by about 1°C as the chiral fraction is increased from 0 to 0·8. The pitch of the cholesteric phase far above $T_{\text{Ch-S}_A}$ of the pure chiral compound was about 0·4 μm. These results are consistent with our results and Lubensky's prediction.

Chirality has many physical manifestations in liquid crystal physics, in some cases rather transparent and, in others, obscured by more dominant effects. In these experiments we were not able to completely clarify the

effect of chirality on the anchoring strength. However, we found that chirality apparently reduces the transition into the smectic A phase, as predicted theoretically by Lubensky.

Note added in proof.—The authors K.A.C. and C.R. are saddened by the death of our friend and colleague Dick Hornreich.

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