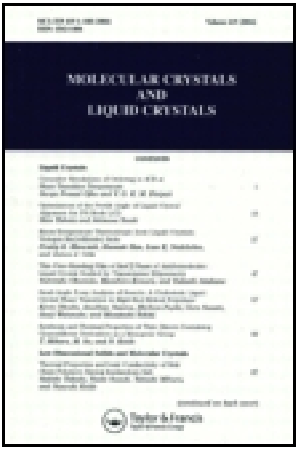

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Ferroelectric Liquid Crystals; A Review

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Ferroelectric Liquid Crystals; A Review†

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The development and the current state of knowledge of ferroelectric liquid crystals are reviewed. Symmetry considerations first indicated that a ferroelectric phase should exist. Synthesis of new molecules led to the first experiments on electro-optical properties, indicating a spontaneous polarization. Various studies of bulk samples, including further electro-optical effects, shear induced polarization, pyroelectric effects, and switching experiments are discussed. Studies of the Curie point and effects visible in freely suspended films are summarized. Comparisons with crystalline ferroelectrics are made. Some further work and possible applications are indicated.

I INTRODUCTION

The study of ferroelectric liquid crystals has been going on for less than three years. In that time, the subject has reached an interesting stage. A remarkable number of the original conjectures on the class of materials[1] have been confirmed, giving one confidence that our general picture of this phase of matter is correct. Many interesting possibilities remain to be explored. In this paper, an attempt is made to review the development of this field, to summarize our current state of knowledge and to indicate some possibilities for the future.

II SYMMETRY

In the early spring of 1974, I realized that by an unusual combination of symmetry properties, smectic C liquid crystals composed of chiral molecules ought to be ferroelectric. This discovery grew out of my attempt, at that

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† Plenary lecture presented at the Sixth International Liquid Crystal Conference, Kent State University, August, 1976.

time, to review the most general possible coupling between polar ordering and spontaneous curvature in liquid crystals.[2] F. C. Frank had pointed out in 1958 that molecular chirality was responsible for the spontaneous torsion of cholesteric liquid crystals, and that a state of uniform torsion of the nematic director field could be achieved by a simple helicoidal structure, filling 3-dimensional space without the necessity of any systematic defect structures.[3] In the same article Frank explored the possible consequences of a spontaneous polarization parallel to the director. In that case, a spontaneous splay curvature is induced, but as Frank indicated, a three dimensional structure containing uniform splay and filling space without defects does not exist. The spontaneous splay could only be achieved in combination with other curvature, in an inhomogeneous structure. The energy associated with these structural complexities could be high enough to prevent the appearance of a spontaneously splayed state as evidence of the presence of polar symmetry along the director. The contrast with a cholesteric is significant; even the slightest chiral perturbation of a nematic produces an observable torsion.

The third case of interest is that of spontaneous bending curvature coupled to a polarization normal to the director, which has been considered in connection with the flexoelectric effect.[4] Is there a space filling structure containing uniform bending of the director field? There is; if one starts with a cholesteric structure, and adds a constant component of the director parallel to the helix axis, the result is a state of uniform torsion and bending, the relative amounts of bend and twist being determined by the tilt angle of the director relative to the helix axis. Since this is the structure of the helix in a chiral smectic C, I realized that in fact there must be a polarization associated with that helix.

Because the spontaneous torsion and bending in the helix, and the associated polarization, are all perturbations of the same order of magnitude, it seemed there must be some fundamental coupling of molecular chirality and polarization in a smectic C system. The idea of preferential orientation of molecules in the smectic C structure, suggested by W. L. McMillan,[5] led me to realize that this coupling of chirality and polarization occurs at the local molecular level, and is independent of the presence of the helix. Although the final result can be stated most clearly in molecular terms, it was Frank's ideas on macroscopic symmetry that stimulated the initial discovery.

The molecular symmetry argument goes as follows. The environment of a molecule in a smectic C structure has monoclinic symmetry (see Figure 1). The general monoclinic cell contains three symmetry elements: a two-fold axis normal to the tilt direction and in the plane of the layers, a mirror plane normal to the two-fold axis, and a center of inversion. If the molecule is chiral, it has no mirror planes or center of inversion. Combining the molec-

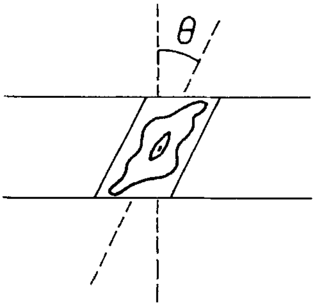


FIGURE 1 Schematic of a low symmetry molecule in a monoclinic symmetry environment.

ular and environmental symmetry leaves the structure with only a two-fold axis. Therefore it is possible to have a spontaneous polarization parallel to the two-fold axis.

A closer look at liquid crystal molecular structures shows that "possible" in the last sentence means "necessary". Non-chiral liquid crystal forming molecules contain at least one mirror plane, for their time averaged structure. This plane is the one to which benzene rings are approximately parallel. They usually contain some polar groups, whose avarage dipole moment must lie in that mirror plane. One simple way of building a smectic C structure out of such molecules is to align their mirror planes with the macroscopic structure's mirror plane. In that case, there is clearly no dipole moment parallel to the two-fold axis. However, if the molecules are chiral they contain no mirror plane. In doing the analogous construction of the smectic C phase out of chiral molecules, there is no symmetry argument to restrict the molecular dipole moment to the plane normal to the macroscopic two-fold axis. In general, the preferred orientation of the chiral molecule in the smectic C environment can include an arbitrary direction for the molecular dipole moment, having some component parallel to the two-fold axis. Therefore, sufficient conditions for polarity of the smectic C phase are that the molecules be chiral and polar. The only remaining question is the magnitude of the spontaneous polarization.

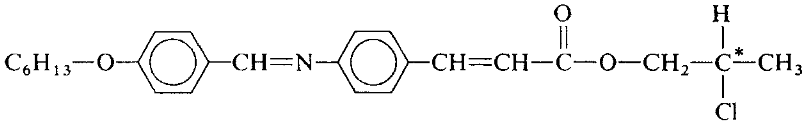
Since the chiral smectic C structure contains a helix as well as a spontaneous polarization, one might ask if it is more appropriate to call it a helical anti-ferroelectric than a ferroelectric. This question is answered in the negative by the following considerations. There are two kinds of molecular interactions involved in forming the helix. First, as in a cholesteric, there is a spontaneous twist due to the molecular chirality. Second, there is a spontaneous bending due to the polar symmetry of the structure. Alone, either of these effects would create a helix as the ground state of the system. Together they may add constructively or compete with one another. Therefore, by varying the thermodynamic conditions, the torsion of the helix could go to zero while the spontaneous polarization remains finite, or vice versa. The easiest way to achieve such a result would be to make a mixture of two chiral smectic C materials exhibiting helices of opposite handedness; at some composition, the pitch may go to infinity, while the two contributions to the polarization do not cancel. In a racemic mixture, however, both the torsion and the spontaneous polarization disappear.

Finally, a contrast must be drawn between these materials and the common crystalline ferroelectrics. The fundamental definition of ferroelectricity requires two properties, spontaneous polarization and the ability to reorient the polarization within the crystal with a small external field. The second condition is satisfied in the liquid crystal by the fluid nature of the ordering in the smectic C layers, allowing easy reorientation of the molecules in response to an applied field. Beyond the practical satisfaction of the definition, however, the liquid crystalline ferroelectrics are quite different from crystalline ones. In the crystalline case, a fundamental electrical and elastic instability is responsible for the appearance of the spontaneous polarization; the associated distortion of the crystal lattice is often extremely small. It is because the distortion is small that the polarization is easily reoriented. However, in the liquid crystal, the fundamental forces responsible for the existence of the smectic C phase have nothing to do with the spontaneous polarization. The molecular tilt angle, corresponding to the mechanical distortion of the crystal lattice, is very large, while the electrical polarization is a small secondary effect. This is just the opposite of the crystalline case, and it has several consequences. For the thermodynamics of the chiral smectic C, one can essentially ignore the presence of the polarization. However, the polarization is large enough to act as a useful "probe" of smectic C, either as a "handle" on the internal structure, which can be controlled by external fields, or as a detector of internal processes, which is strong enough to generate measurable external fields. Examples of these cases will be discussed below.

III MOLECULES

Once the symmetry arguments for ferroelectricity became convincing, the choice of appropriate systems for exprimental study was important. Lionel Liébert and I began discussing the problem, and eventually L. Strzelecki and Patrick Keller became involved as well. Our first thought was to find a material, exhibiting a smectic C phase at a reasonable temperature, which could be modified slightly to be chiral, and which could be made quickly and easily. The choice of active amyl-(*p*-(*p*-decyloxybenzylideneamino))cinnamate (DOBAMBC) proved successful.[1]

In speculating on the magnitude of the spontaneous polarization to be expected, we considered two problems. First, the interaction of the molecule with its monoclinic symmetry environment might be very weak, so that the molecule might be almost freely rotating about its long axis, with only a minute polar bias. This is a fundamental problem, difficult to act upon by changing the molecular structure without losing the probability that a smectic C phase would exist. Second, although the chiral part of the molecule might be preferentially oriented in a polar way, internal rotations might leave it only weakly coupled to the polar groups on the molecule. Our initial choice of molecule seemed somewhat deficient in this respect, since the chiral group is not itself very polar. The validity of this second concern seems to have been demonstrated convincingly in the last few months. Keller, Liébert, and Strzelecki have synthesized a chiral smectic C molecule:



in which the assymetric carbon atom has a highly polar chlorine atom attached directly to it.[6] The spontaneous polarization in this material is ten times larger than that observed in a number of other compounds, all containing purely hydrocarbon chiral groups. As for the first concern, it still appears to be important; none of the materials studied appears to have a spontaneous polarization of more than a few percent of the total molecular dipole moment.[7] This is consistent with the picture of the spontaneous polarization as a small perturbation of the smectic C structure.

IV BULK PROPERTIES

The initial objective of experimental work on the newly synthesized materials was a clear test for the presence of spontaneous polarization. In discussions with Georges Durand, Irl Smith, Yves Galerne and Roland Ribotta, several ideas were considered, which will be returned to below. I decided to try first electro-optical studies of single domain samples. These experiments demonstrated a linear response to an applied field, strong evidence for a spontaneous polarization.[1]

However, an even more convincing test would be one not involving any applied electric field, but detecting the presence of the polarization by a direct electrical measurement. In discussing the possibilities for mechano-electrical effects, Liliane Léger pointed out that there should be a linear coupling between shear flow of the smectic layers over one another and the orientation of the tilt direction in the layers. This would result in a shear induced polarization normal to the shear velocity. During 1974–75, Pieranski, Guyon, Keller and Liébert carried out this experiment successfully at Orsay, providing an elegant demonstration of the reality of the spontaneous polarization.[8]

Two other experiments on bulk samples have given further evidence for the case. First, the group at Temple University led by M. M. Labes demonstrated a pyroelectric effect in the chiral smectic C phase.[9] Second, Martinot-Lagarde at Orsay has now measured the polarization-associated switching current, produced when a sample is poled in an applied field, and the field polarity is suddenly reversed.[10] This experiment is the first one which can claim to measure directly the magnitude of the spontaneous polarization.

Understanding the bulk properties of the ferroelectric smectic C is mainly understanding the behavior of the helicoidal structure. It plays the role of a domain structure in a crystalline ferroelectric, to the extent that such an analogy is applicable. Of course, the source of the helix is quite different from that of ferroelectric domains. It arises from local interactions rather than the minimization of the macroscopic electrostatic field energy.

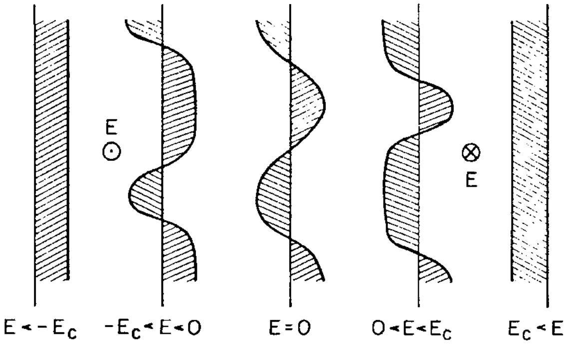


FIGURE 2 Response of the helix to an electric field.
(R. B. Meyer, Mol. Cryst. Liq. Cryst., 40, 33-48, 1977.)

Figure 2 indicates schematically the response of the helix to an electric field applied in the plane of the layers. Below a critical field, E_c, the helix is distorted so that the regions in which the polarization is favorably oriented grow. This produces a preferred tilt of the molecules in one direction, normal to $\bar{E}$. Above E_c, the helix is unwound, and the sample is poled. Reversing the sign of E reverses the polarization and the direction of molecular tilt.

The critical field can be calculated in formal analogy with the calculation of the simple dielectric alignment effect in a cholesteric.[11] The dielectric interaction term, $-(\Delta\varepsilon/8\pi)(\bar{E}\cdot\hat{n})^2$ for the cholesteric, is replaced by $-\bar{E}\cdot\bar{P}$

in the ferroelectric. The free energy density is therefore:

$$g = \frac{1}{L}\int_0^L \left[\frac{1}{2}K\left(\frac{\partial\phi}{\partial z} - t\right)^2 - \bar{E}\cdot\bar{P}\right]dz \tag{1}$$

By a change of variable, doubling the phase angle ϕ and torsion t of the smectic C helix, one obtains a free energy of the same form as that for the cholesteric, with the result that:

$$E_c = \frac{\pi^4 K}{4LP} \tag{2}$$

For practical values of the torsional elastic constant K (10^{-7} dynes), helix pitch L(1 μm), and polarization density P (100 esu/cm^2), E_c is of the order of a few hundred to a few thousand volts/cm. In general, if P were very small, one would have to consider combined ferroelectric and dielectric alignment effects. In cases studied so far, however, P is large enough so that this is unnecessary. On the other hand, if P were very large, one would have to consider the possibility of modification of the uniform applied electric field by the spontaneous polarization. In the general case, the helix need not respond to the applied field uniformly. A first order transition in which sections of the helix would unwind, and other parts would remain coiled would be possible. Again, this has not been observed. Therefore, the simple calculation of the response presented here seems adequate.

The time dependence of the ferroelectric alignment effect is governed by a rotational viscosity γ. The relaxation frequency τ^{-1} for distortion of a helix of torsion t is:

$$\tau^{-1} = \frac{Kt^2 + E\cdot P}{\gamma}.$$

For electric fields of the order of E_c or less, τ^{-1} is a few hundred Hertz. Since the linear response requires P to follow E, the ferroelectric alignment effect is limited to low frequencies. Ordinary dielectric alignment persists at high frequencies, since it depends on $\langle E^2\rangle$ which contains a static component independent of frequency. This provides a useful mechanism for comparing ferroelectric and dielectric alignment, which has been used to confirm the dominance of the former effect when it is present.[1]

Another aspect of the ferroelectric response to an applied field is hysteresis. In crystalline ferroelectrics, in which there may be only a few easy axes for polarization, domain walls can have a high energy, due mainly to crystalline anisotropy. The pinning of domain walls, or the difficulty of nucleating new ones, is a major cause of hysteresis effects. In a single crystal chiral smectic C, there is no easy axis for polarization in the smectic layers, and thus there are no spontaneous domains; only line defects are allowed. Therefore in principle hysteresis is not possible. However, in polydomain samples, or very thin ones contained between surfaces with strong alignment anchoring, there can be pinning effects which produce at least partial hysteresis. This is easily observed in experiments involving unwinding of the helix. When E is reduced below E_c, the helix reappears non-uniformly by the generation of discrete twist walls which nucleate on defects. At $E = 0$, the equilibrium pitch may not be achieved after such an experiment.

There are several optical methods for observing the distortion and unwinding of the helix. The one employed first experimentally was observation of the conoscopic image.[1] Starting with a homeotropically aligned sample in the A phase, and cooling slowly into the C phase, one achieves a single domain with the helix axis normal to the glass slides containing the sample. The conoscopic image of such a sample has uniaxial symmetry, due to the presence of the helix. In the center of the image, for light propagating along the helix axis, there is a strong optical rotatory power. Off axis, one sees a series of rings and a crossed brush pattern, indicating that the propagating optical modes approach the linearly polarized modes of an ordinary uniaxial crystal. The crossover from circularly to linearly polarized modes has not been studied in detail.

Applying an electrical field in the plane of the sample, via wires imbedded in it, one observes a sequence of change on the conoscopic image. At low E, there is a shift of the pattern, linear in voltage, in a direction normal to $\bar{E}$. This corresponds to the distortion of the helix, in which the molecular axis and optical axis are biased in one orientation. As a second order effect, the circular rings in the image distort to an elliptical shape. Above E_c, the image becomes biaxial, as expected for an oriented smectic C, and the pattern ceases to change as E is increased further. The helix is unwound and the sample is poled. Reversing the sign of E reverses the direction of the initial shift and the orientation of the final biaxial pattern. This was the first unambiguous evidence of a linear response to an applied field, and therfore of the existence of spontaneous polarization.

For an estimate of the polarization density, one can measure both E_c and the helix pitch; this determines K/P. A convenient geometry for this experiment is one in which the helix axis lies in the plane of the sample, so the smectic layers are normal to the glass slides, and the electric field is applied in the plane of the layers by tin oxide electrodes on the glass. One can resolve the periodic structure of the helix with a microscope, and determine E_c accurately. This provides a good estimate of P, although hysteresis effects make the pitch of the helix difficult to measure accurately. Since both K and P depend on the magnitude of the smectic C tilt angle θ, one should compare measurements on different materials after normalizing for this dependence. R. Duke and G. Durand did extensive measurements of the temperature dependence of θ and K/P for materials synthesized at Orsay.[7] Since K varies as θ^2 and P as θ, for small θ, one expects the same temperature dependence for θ and K/P, which is what Duke and Durand found.

A third method for optical detection of the electric field effects is one beginning to be studied at Harvard. It is the observation of Bragg scattering by the helix, and its electrical modulation. In cholesterics, the dielectric alignment effect is weak enough so that one needs very high electric fields to achieve interesting color effects in the visible range of the spectrum. In the ferroelectric smectic C, this is not so, as materials with helix pitch in the visible range are developed, some spectacular effects may be possible with relatively low fields.

Although electro-optical properties of these material will continue to be the most fascinating for many purposes, some non-electrical experiments were needed for a completely convincing demonstration of the presence of a spontaneous polarization. The general prescription for such an experiment is an applied force which couples linearly to the molecular tilt direction, which could be used to distort or unwind the helix, producing a macroscopic polarization in the sample, which would be detected electrically. One candidate for this force, which has now been tried, is shear flow.[8]

A second appropriate force for linear coupling to the molecular orientation is a magnetic field applied obliquely to the smectic layer normal. This possibility was discussed in detail by Irl Smith, but the experiment has not been tried.

Finally, an experiment of a different nature from the proposed prescription given above is one suggested by Yves Galerne, In a sample which has been poled by some previous treatment, one could apply stress normal to the smectic layers, modulating the magnitude of the tilt angle and also changing P. This would induce a voltage on appropriately located electrodes. This effect would be the direct analogue of the effect utilized in crystalline piezoelectric transducers constructed of ferroelectric material. The inverse effect might also be possible in the ferroelectric smectic C. Studies of these effects have not yet been performed, but they could lead to interesting applications of these materials.

V THE CURIE POINT

In a number of the materials studied to date there is an apparently second order smectic C–smectic A transition, at which both θ and P go to zero continuously as temperature is raised to the transition temperature, T_c. Although the forces driving the phase change are not primarily associated with the existence of the spontaneous polarization, nevertheless, since P goes to zero at T_c, this is a Curie point, and it exhibits properties similar to the Curie point in materials in which the transition is primarily an electro-elastic instability. This is true because, although P is not the primary order parameter for the transition, it is linearly related to the primary order parameter, which we will take as θ, for simplicity.

To see some properties of the Curie point, one can write down a mean field expression for the free energy of the material, above T_c, involving P, θ, and an electric field E applied in the plane of the smectic layers. P is the part of the polarization, induced by E, that can be attributed to the fixed molecular dipole moments, and it is parallel to E. θ is a tilt angle in a direction normal to E and P. For now we will ignore the possible effects of the spontaneous helical torsion that appears below T_c. The free energy density is then:

$$F = F_0 + \tfrac{1}{2}A\theta^2 + \tfrac{1}{2}\chi^{-1}P^2 - PE - \frac{1}{8\pi}\varepsilon^0E^2 - t\theta P. \qquad (3)$$

The first two terms are the beginning of the Landau series expansion in terms of θ, and $A = a(T - T_c)$. The next three terms are the usual ones describing the electrostatic free energy. ε^0 is a dielectric constant due to sources other than the fixed molecular dipoles that contribute to P. The last term represents the lowest order coupling between P and θ. In principle, one could include a term bilinear in E and θ, but we assume that all interaction of E with θ is mediated by the induced polarization P. First, minimizing F with respect to P, by setting $\partial F/\partial P = 0$, we find:

$$P = \chi(E + t\theta). \qquad (4)$$

In the absence of the coupling to θ, χ would be the dielectric susceptibility due to P. This equation shows that if we apply a force which produces a finite θ, say by shearing the smectic layers over one another, a finite P will result, even for $E = 0$.

Substituting for P, we have:

$$F = F_0 + \tfrac{1}{2}(A - \chi t^2)\theta^2 - \chi tE\theta - \frac{1}{8\pi}(\varepsilon^0 + 4\pi\chi)E^2 \qquad (5)$$

The extra term χt^2 in the coefficient of θ^2 represents a shift in the transition temperature due to the coupling of P and θ. For simplicity, we now set $A' = (A - \chi t^2)$. We also see that the dielectric constant has been augmented by $4\pi\chi$, as expected. Since we eliminated P by setting $\partial F/\partial P = 0$, while holding θ constant, this correction to ε does not exhibit any pretransition effect. Now, viewing E as the only independent variable, and setting

$\partial F/\partial\theta = 0$, we find:

$$\theta = \frac{\chi t E}{A'}. \tag{6}$$

The field induced tilt diverges at T_c, as A' goes to zero. This suggests an experiment in which θ is measured optically, while temperature and the frequency of the applied field are varied, to determine the pretransition behavior of A', which is discussed below. Finally, substituting for θ, we find:

$$F = F_0 - \frac{1}{8\pi}\left(\varepsilon^0 + 4\pi\chi + 4\pi\frac{(\chi t)^2}{A'}\right)E^2. \tag{6}$$

The coupling of E to θ produces a divergent component of ε, as expected at a Curie point. This effect has been observed by R. Duke and G. Durand at Orsay.[12]

This simple analysis was made with the assumption that P is a small perturbation. This assumption means that the change of T_c due to the coupling of P and θ is small. One test of this idea is made by comparing T_c for a racemic mixture, which is not ferroelectric, with T_c for the pure chiral version of the same material. Experimentally, the two temperatures cannot be distinguished, in the face of variations due to impurities. One could argue that the racemic mixture is not really non-chiral, but rather corresponds to an antiferroelectric, with two molecules per unit cell. If the molecular interactions are very short range, then the change of T_c due to the chirality of the individual molecules might be the same in the racemic and pure chiral materials. A truer test would be the continuous change of the chirality of the individual molecules, which is physically unachievable.

Ignoring the helix torsion is not too serious above T_c, since fluctuations will only be greatly modified by torsion when the coherence length becomes comparable to the helix pitch. However, when that happens, the simple field-induced-tilt effect will no longer be divergent, and likewise ε will not contain a true divergence at T_c. Within a very small temperature range near T_c the response will resemble an antiferroelectric, rather than a ferroelectric. Of course, the finite torsion within the fluctuations will directly affect chiral properties such as optical rotatory power, as is seen above the isotropic–cholesteric transition. Below T_c, the role of the helix is more complex, and has not been studied in detail.

With the view of P as a convenient and innocuous probe of the smectic A–smectic C transition, the field induced molecular tilt experiment, implied by Eq. 6 above, has been performed at Harvard.[13] The field induced tilt angle θ corresponds to a rotation of the optical axis of a single crystal sample. This is measured by monitoring the birefringence of the sample with a laser beam propagating at an oblique angle to the optical axis. Adjusting the angle of incidence so that one is operating around one of the half-intensity points in the conoscopic ring pattern, the change of intensity observed is linear in θ. By the use of phase sensitive detection, one can easily measure θ in the microradian range. Both the amplitude of θ and its phase in time, relative to an applied a.c. field, can be used to determine the temperature dependence of A'. The natural relaxation frequency of θ is expected to vary as $\nu = A'/\eta$, in which η is a rotational viscosity which should show very weak or negligible pretransition behavior. Experiments so far bear out this simple picture of the transition.

The smectic A–smectic C phase change has been compared to the superfluid transition in liquid helium.[14] The temperature dependence of A' above T_c is described by a critical exponent γ, which is 1.0 according to mean field theory, and 1.315 if the analogy with helium is valid. The preliminary value of γ determined in these experiments is approximately 1.11, between the two limiting values. The electro-optical response within about 20 mK of T_c deviates from the simple theory, and its explanation is still obscure. However, the use of the ferroelectric polarization as a probe has provided some of the first precise experimental data on this phase change.

VI FREELY SUSPENDED FILMS

An unusual although convenient sample geometry for studying smectic liquid crystals is that of a thin film supported only at its edges, stretched like a soap film over a hole in a solid substrate. G. Friedel looked briefly at this kind of sample, and the group at Harvard is making extensive studies of such samples.[15] This has proved to be an especially useful technique for the study of ferroelectric smectic C liquid crystals.

With the film stretched over a rectangular hole in a glass cover slide, and metal electrodes vapor deposited on the long edges of the hole, one can apply a field of a few volts/cm. in the plane of the layers, and achieve a uniformly aligned sample. By rapidly switching the polarity of the field one often creates domain walls across which the director rotates by 2π radians. These can be studied by polarized light reflection microscopy. Ronald Pindak and Charles Young have done detailed studies of the structure of such walls and its variation with respect to voltage and orientation, as well as the collapse rate of wall loops, which gives information on the rotational viscosity of the smectic C phase.[16]

In the absence of an applied field, there is no evidence of spontaneous domain formation in the ferroelectric films studied, which are typically in the range of two to ten molecular layers thick. Point disclinations are commonly observed, around which the director and P rotate by 2π radians. With a small applied field, the quasi-uniform rotation about a point disclination is compressed into a single wall, a few tens of microns in width, terminating at the point. One can understand the structure of such a wall from a simple model, which is closely analogous to that for alignment inversion walls induced in a nematic by a magnetic field.[17] Assuming a single splay-bend elastic constant, one can write a free energy per unit length of wall as:

$$F = \int_{-\infty}^{\infty} \left[\frac{1}{2} K \left(\frac{\partial \phi}{\partial x} \right)^2 - \bar{P} \cdot \bar{E} + PE \right] dx \tag{8}$$

in which ϕ is the phase angle of the two dimensional director, and x is a coordinate normal to the wall. Again, by a change of variable from ϕ to 2ϕ, the problem becomes formally equivalent to the familiar magnetic alignment problem. The wall width, defined as the distance between the $\pi/2$ and $3\pi/2$ rotation within the wall, varies as:

$$w = 1.76 \left(\frac{K}{PE} \right)^{1/2} \tag{9}$$

Again using the typical values of K and P, one finds that for E a few volts per cm, w is a few tens of microns, as is observed. The variation of w as $E^{-1/2}$ is also confirmed experimentally.

One can think of significant corrections to this model of the wall, due to three effects. First, different splay and bend elastic constants introduce a small anisotropy in the structure, which may be detectable. Second, there should be a spontaneous bend term, which would show up as a polarity in the wall structure, making the two halves of walls of one orientation have different widths. This may be too small an effect to observe. Third, the electrostatic self energy of a wall could be taken into account, but this has not been done yet.

Circular wall loops appear to be quite uniform in their structure, supporting the simple model presented above. They shrink very slowly under their line tension driving force. One can therefore use a quasi-static model, worked out by Ronald Pindak, for their collapse rate.[16] One simply equates the net change in static wall energy with radius to the energy dissipated by rotational viscosity as the wall moves. This results in a collapse rate for the radius R:

$$\frac{dR}{dt} = -\frac{K}{\gamma R} \tag{10}$$

in which γ is an effective rotational viscosity. The rate is independent of the applied field. Experimental results are in agreement with this model.

The switching behavior of the thin film containing numerous domain walls is interesting. The polarization along the center line of each wall is aligned opposite to the applied field before switching. After a rapid change in polarity of E, this region is favorably aligned, and grows in width. The wall splits into two halves which move apart. If neighboring walls are of the same sense of rotation, the two half walls moving toward one another recombine to form a new wall midway between the original pair.

The second important application of these thin film samples has been in the study of thermally excited orientation fluctuations, by light scattering. Using a small in-plane electric field to align the sample uniformly, one can then look at light scattered by the bend and splay director modes separately. Since the two dimensional director and the spontaneous polarization are perpendicular to one another, the splay mode of the director is the mode for which $\nabla \cdot \bar{P} = 0$. This mode exhibits ordinary curvature elasticity; no unusual behavior due to the two dimensional character of the sample has been seen. For the director bend mode, $\bar{\nabla} \cdot \bar{P} \neq 0$, and there is an electrostatic part of the free energy for these fluctuations due to the polarization dependent space charge. For a two dimensional charge distribution, with the electric field of course propagating in three dimensions, this results in a part of the free energy density which varies as the absolute value of the wave vector, as opposed to the elastic part which depends on the square of the wave vector. This behavior has been measured experimentally by Charles Young and Noel Clark.[18] The determinations of K/γ made by the study of the domain walls and independently by light scattering are in good agreement. From the domain wall studies, one can determine K/P, and from light scattering one gets K/P^2. These agree with one another if P is of the order of a few hundredths of a Debye per molecule.

VII OTHER POLAR PHASES

The symmetry argument showing that the smectic C phase composed of chiral molecules is polar applies equally to any monoclinic or triclinic structure, for example, the so-called smectic H or tilted B phase, and crystals.

In DOBAMBC, the smectic H phase exhibits some striking properties. It appears to contain a stable helicoidal structure like that of the C phase. Moreover, it exhibits electro-optical response like that of the C phase, but with a very long relaxation time, which varies significantly with temperature near the smectic H–smectic C transition.[1] In the freely suspended film samples, disclinations and domain walls present in the C phase are "frozen in" in the H phase, but still move slowly in response to small in-plane electric fields.[19]

There has been some speculation[20,21] and several experiments on the smectic B and H phases, which are quasi-crystalline. The behavior described above is surely not compatible with ordinary crystal structure. Since the molecular tilt direction should bear a unique (6-fold degenerate) relationship to the orientation of the crystal lattice believed to exist in this phase, the observed continuous rotation of the tilt direction should indicate that the local lattice rotates with the tilt direction. In ordinary crystals this would be accomplished by a series of sharp grain boundaries. In the smectic H phase, this may be accomplished by a uniform distribution of dislocations. In analogy with superconductors, following De Gennes's discussion of the smectic A phase, this tendency for dislocations to remain uniformly distributed could be called type II behavior.[22] It can arise when the curvature elastic moduli associated with the "director" or tilt direction become large enough, compared to the first order elastic moduli associated with ordinary strain of the lattice. Whether or not this is the case for the chiral smectic H phase, its plastic flow properties allow it to be classified as a ferroelectric.

In the case of monoclinic or triclinic molecular crystals, it is unlikely that the polarity associated with molecular chirality will result in ferroelectric properties. However, such crystals should be pyroelectric and piezoelectric, and some exploratory experiments on such materials could easily be done.

VIII FUTURE POSSIBILITIES

So far, the initial speculations about the chiral smectic C phase, based on symmetry arguments and some simple ideas about molecular structure, have been remarkably well confirmed by experiments. However, most of the experiments have been aimed at qualitative examination of various phenomena. In the case in which careful quantitative work has been done, new questions have been raised by the results, which remain to be pursued. The study of the Curie point is an example. The nearly mean field nature of the pretransition effects above T_c is unexplained. The role of the helical torsion in the transition is also unresolved.

The potential applications of the electro-optical effects in the ferroelectric phase have only begun to be explored. Especially interesting are the possible switching effects in very thin layers between conducting glass plates, in which surface pinning effects may be utilized to achieve an electro-optical memory. The electrically modulated Bragg scattering or birefringence or optical rotatory power may also find useful applications.

Finally, the development of new materials clearly offers promise. Large spontaneous polarization, a helix pitch in the visible range, a convenient temperature range for the smectic C phase, are all goals to be added to the usual demands for chemical stability and desirable electrical, optical, and surface alignment properties that are familiar in other programs of liquid crystal materials development.

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