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FERROELECTRIC LIQUID CRYSTALS

R. B. MEYER (*), L. LIÉBERT, L. STRZELECKI and P. KELLER

Université Paris-Sud, Physique des Solides (**), 91405 Orsay, France

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Résumé. — Un argument général de symétrie est présenté et des expériences sur le p-décyloxybenzylidène p'-aminocinnamate de méthyl-2 butyle sont décrites démontrant que les smectiques C et H chiraux sont ferroélectriques. Quelques propriétés de cette nouvelle famille de ferroélectriques sont discutées.

Abstract. — A general symmetry argument is presented, and experiments on newly synthesized p-decyloxybenzylidene p'-amino 2-methyl butyl cinnamate are described, demonstrating that chiral smectic C and H liquid crystals are ferroelectric. Some of the properties of this new class of ferroelectrics are discussed.

In spite of speculation on the possibility of ferroelectric liquid crystalline phases [1], there has never been a compelling fundamental reason for, or experimental demonstration of the existence of ferroelectricity in these systems. In this letter we show by symmetry that smectic C and H liquid crystals composed of chiral molecules must have a spontaneous polarization. The synthesis of a new material exhibiting these phases is reported, and experiments are described which determine the existence and approximate magnitude of the spontaneous polarization. Some of the unusual properties of these fluid ferroelectrics are discussed.

In a smectic C liquid crystal, rod-like molecules are arranged in layers, with the long molecular axes parallel to one another and tilted at an angle θ from the layer normal. Each layer is a two-dimensional liquid. In the smectic H phase (also called tilted B), the molecular layers are crystalline; there remains some question about the degree of correlation of the lattices on different layers. These properties are well established by x-ray [2] and optical studies [3].

Both these phases have monoclinic symmetry, the point group for which contains only a two-fold rotation axis parallel to the layers and normal to the long molecular axis, a reflection plane normal to the two-fold axis, and a center of inversion. However, if the phase is composed of chiral molecules (not

superposable on their mirror image) then the mirror plane and the center of inversion are eliminated. The remaining single two-fold axis allows the existence of a permanent dipole moment parallel to this axis.

The typical liquid crystal molecule has a permanent dipole moment and is of low enough symmetry so that it has only two degenerate minimum energy positions in a monoclinic environment, connected by the two-fold rotation. If the molecule is non-chiral, the mean orientation of its permanent dipole must be normal to the two-fold axis. However, the skewed form of a chiral molecule forces the permanent dipole to have a component parallel to the two-fold axis. If all the molecules are identical this produces a net polarization of at most a few Debye per molecule. A racemic mixture, however, will have no net polarization.

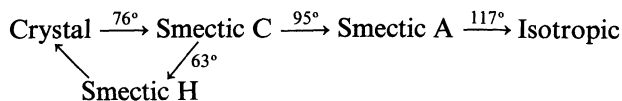
Two effects tend to reduce the magnitude of the spontaneous polarization. First, the coupling of the molecule to the monoclinic environment may be weak, so that the molecule is almost freely rotating about its long axis. Second, if the chiral part of the molecule is only weakly coupled to the polar part, then internal molecular rotations may reduce the polarization.

With these considerations in mind, a new chiral material, p-decyloxybenzylidene p'-amino 2-methyl butyl cinnamate (DOBAMBC), was synthesized. By analogy with similar molecules it was expected to have a smectic C phase, and because the chiral 2-methylbutyl group is next to the polar ester group, it was hoped that the problem of internal rotation would be minimized. The thermal phase diagram

(*) Alfred P. Sloan Foundation Research Fellow. Present address, Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts, U.S.A. 02138.

(**) Laboratoire associé au CNRS.

was determined by polarized light microscopy and x-ray studies :



The smectic C \rightarrow smectic A transition appears, by differential scanning calorimetry and optical measurements, to be second order, with θ going continuously to zero, while the other transitions are first order.

In both the C and H phases, a helicoidal structure is observed, in which the molecular tilt direction precesses around the normal to the layers, with a pitch of several microns. There are two causes for this helix. First, as in a cholesteric liquid crystal, there is a chiral component to the intermolecular interactions which induces a spontaneous twist in the ground state structure [4]. Second, the same symmetry argument that predicts a spontaneous polarization also requires in the ground state a spontaneous bending curvature [5]. In fact, this helicoidal structure is a state of uniform torsion and bending of the molecular alignment. (This was expected for the smectic C phase [6], but it raises fundamental questions about the H phase to which we will return later); because the helix results from two different interactions, it should be possible to find conditions where, in a pure material, the helix disappears (pitch $\rightarrow \infty$), while the spontaneous polarization does not. Another way to get the same situation could be to mix different materials, compensating for the pitch but not for the local dipole.

To detect the spontaneous polarization, the electro-optical properties of DOBAMBC were examined. First, samples were prepared between glass plates treated with hexadecyltrimethyl ammonium bromide, which induces the smectic planes to lie parallel to the glass, in the smectic A phase. Upon cooling into the C phase, this ordering is preserved. The electric field was applied parallel to the layers between a pair of 200 μm diameter copper wires imbedded in the sample 1.5 mm apart; the wires also served as spacers for the glass.

For these samples, the conoscopic image was observed, using crossed linear polarizers. With no field, due to the presence of the helix a uniaxial interference figure was seen, centered on the layer normal, and consisting of a series of concentric rings, just as in the A phase, and an extinction cross, the center part of which is more or less distinct, depending on the molecular tilt angle. With a small applied field, this figure shifts, without apparent distortion, in a direction normal to the field. This effective rotation of the macroscopic optical axis is linear in the field, changing direction when the field is reversed. At higher fields, the helicoidal structure is completely unwound, with the molecular tilt direction uniformly oriented normal to the field, producing the typical biaxial interference

figure of a monodomain smectic C sample. Again, reversing the field reverses the tilt direction.

This behavior is consistent with ferroelectric coupling. At high field the polarization is uniformly aligned, producing the observed monodomain structure. The low field behavior results from distortion of the helix, in which regions of favorable polarization grow at the expense of the intervening regions of opposite polarization. This shifts the mean optical axis toward the high field direction. The helix serves as an ideal ferroelectric domain structure, although it arises from local, not long range, interactions.

For quantitative measurements, the ferroelectric coupling must be separated from the ordinary dielectric coupling due to the anisotropy of the dielectric constant [7]. Since the ferroelectric coupling requires the tilt direction to rotate with the field, this response is damped by the rotational viscosity of the fluid, and in practice disappears above a few hundred Hertz. The dielectric coupling, which is quadratic in field, produces a static response which persists at high frequency.

By preparing samples between glass slides coated with transparent tin oxide electrodes, a focal conic texture is obtained in which the applied field is again parallel to the smectic layers, in some regions. In these regions, the helix produces a series of parallel stripes, allowing direct measurement of the pitch and the critical field E_c for unwinding the helix. The high frequency value of E_c was typically at least a factor of 20 higher than the d.c. value, meaning that the dielectric coupling can be ignored at low frequency. The ferroelectric coupling results in a critical field $E_c = \pi^4 K/(4lP)$, in cgs units, with l the full pitch of the helix, P the polarization, and K a torsional elastic constant for the helix [8]. Using measurements at 86 $^\circ\text{C}$, $E_c = 2400$ V/cm, and $l = 1.5$ μm . Estimating $K \simeq 10^{-6}$ dyne, then $P \simeq 125$ statcoul./cm², or about 0.25 Debye/molecule, which is not unreasonable; estimating the anisotropy of the dielectric constant $E_a/4\pi \sim 1$, the electric polarization induced by E_c (~ 8 cgs) is much smaller than our estimated value for P , showing the consistency of our interpretation. E_c varies from 600 V/cm at 94 $^\circ\text{C}$ to 6500 V/cm at 63.5 $^\circ\text{C}$. The pitch varies from 3 μm at 94 $^\circ\text{C}$ to 1 μm at 73 $^\circ\text{C}$, below which it was too small to be measured in this experiment. Unfortunately, K is not known, so that P cannot be determined.

The properties described above are the most important for classifying a material as a ferroelectric, namely the presence of a spontaneous polarization which is easily oriented by an applied field. The analogy with crystalline ferroelectrics extend further than this. The smectic A \leftrightarrow smectic C transition of DOBAMBC is actually a Curie point.

This transition is driven by intermolecular forces producing the tilt, and not by the ferroelectric coupling [1, 9]. This is confirmed by comparing the transition temperature T_c of the chiral and racemic versions

of DOBAMBC, which differ by less than 1 °C. The situation is then fundamentally different from what happens in usual ferroelectric transitions in solids, where dipole-dipole interactions are directly responsible for the phase change. By symmetry, then, the polarization P is proportional to θ , going to zero continuously at T_c . The linear coupling of P and θ also produces a piezoelectric effect in the smectic A phase. Shear of the smectic layers over one another produces tilt [10] which in turn produces a polarization transverse to the shear. Conversely, an electric field in the plane of the layers produces a polarization and therefore a tilt normal to the field. The latter effect is easily observed in DOBAMBC, although quantitative measurements have not yet been made. As the Curie point is approached from above, the piezoelectric coefficients diverge, which also leads to a divergent dielectric constant.

The molecular tilt mode plays the role of a soft optical phonon at the transition. In this case it is an overdamped mode, and its viscous relaxation frequency tends toward zero at the transition. This should be observable in electro-optic or dielectric constant measurements.

Ferroelectric liquid crystals should have a number of unusual properties. An ordinary smectic C material exhibits curvature elasticity for spatial gradients of the tilt direction, much like a nematic liquid crystal [4, 11]. The presence of the ferroelectric polarization fundamentally alters this situation, since any divergence in P produces space charge and long range coulomb interactions. A bending mode of the tilt direction, with wave vector q parallel to the smectic layers, is a divergence mode of P . The electrostatic energy of this mode is independent of q , in contrast to the elastic energy which varies as q^{-2} . The electrostatic interaction therefore makes this a non-hydrodynamic mode with finite relaxation frequency at zero wave vector. The role of ionic impurities will further complicate the problem.

Another unusual effect will be flow induced polarization. As pointed out by L. Léger, shear of the layers over one another will distort the helix, producing a preferred alignment of the molecules and therefore a polarization transverse to the flow. A similar distortion and polarization can be induced by a magnetic field obliquely oriented to the layer normal. We are grateful to I. W. Smith for a very useful discussion of such an experiment.

The smectic H phase presents fundamental structural problems. The observed helicoidal structure is incompatible with a three dimensional lattice, suggesting that the two dimensional lattices in the smectic layers rotate with the tilt direction in the helix [12]. This requires weak coupling between the layers, and perhaps an equilibrium network of screw dislocations. The electro-optical effects seen in the C phase are observable in the H phase as well, but with a much longer relaxation time, varying from about a tenth of a second near the smectic H-smectic C phase change to several seconds at lower temperatures. The mechanism of the apparently uniform rotation of the tilt direction in response to an applied field may involve the motion of dislocations within the lattice of each layer.

In conclusion, we have demonstrated the existence of a new class of ferroelectric materials. Their unusual combination of fluid and ferroelectric properties leads to some novel phenomena. The ferroelectric and piezoelectric properties of these materials should provide useful probes for the study of their phase changes and their basic structure.

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