

⁷A configuration in which hexagonal domains are oriented parallel to the graphite hexagons, with a phase shift of two sites across a wall, gives peaks at Q_{comm}

$+\epsilon$ and $Q_{\text{comm}} - \frac{1}{2}\epsilon$. These occur at the same places in reciprocal space as the spots observed by LEED (Ref. 1).

Wall-Induced Pretransitional Birefringence: A New Tool to Study Boundary Aligning Forces in Liquid Crystals

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A wall-induced birefringence in a nematic liquid crystal above the nematic-isotropic phase transition point has been observed for the first time. It is expected that this phenomenon will provide a useful tool to study the nature of aligning forces at liquid-crystal-solid interfaces.

It is well known¹ that by a suitable treatment of a substrate surface, one can impose a specific director orientation in a liquid crystal (LC) film. It is supposed that the wall aligns the adjacent LC molecules by exerting anisotropic forces of some physicochemical nature; the bulk of the film is then aligned as a result of the director elasticity.² The wall, thus, acts as an external field and therefore will induce birefringence above the nematic-isotropic phase transition temperature (T_c) just as a magnetic, electric, or shear-flow field does. In this Letter, the first observation of the wall-induced birefringence is reported. The effect is naturally very sensitive to differences in orienting force and is expected to be a useful tool to study the microscopic origin of the aligning forces at LC-solid interfaces.

A wall-induced alignment in the isotropic phase of nematics has been previously analyzed theoretically.³ A simple sketch of the treatment using the Landau-de Gennes theory is appropriate here. The Landau-de Gennes free energy density is given by⁴

$$F = F_0 + F_1(Q) + \frac{1}{2}L|\nabla Q|^2, \quad (1)$$

where

$$F_1(Q) = \frac{1}{2}AQ^2 - \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4, \quad (2)$$

where F_0 is that part which does not depend on the order parameter, Q . It is usually assumed⁴ that $A = a(T - T^*)$ and a together with B , C , L , and T^* are material constants. When the wall imposes some orientation on the LC molecules, the order parameter at the wall, Q_b , is not zero even above T_c . Let us take a Cartesian coordinate system where $z = 0$ defines the wall and the

z axis points into the LC. With the assumption that Q depends only on z , the minimization of the volume integral of Eq. (1) yields

$$\xi_0^2(dQ/dz)^2 = f(Q), \quad (3)$$

with $Q(z=0) = Q_b$ and $Q(z=\infty) = 0$; here $\xi_0^2 = L/aT^*$ and $f(Q) = F_1(Q)/aT^*$. In Eq. (3) it is assumed that the sample is thick enough so that the effect of the other side of the film is negligible.⁵ In the first approximation, the phase difference, $\Delta\varphi$, of the ordinary and extraordinary rays due to the birefringence of the film is proportional to

$$\Delta\varphi \sim \int_0^\infty Q(z)dz. \quad (4)$$

Equation (4) was calculated numerically using a set of parameters pertinent to pentyl-cyanobiphenyl (5CB) from Coles⁶ and assuming $\xi_0 = 6 \text{ \AA}$.⁷ The result is shown in Fig. 1 for different values of Q_b as a function of temperature. The sudden increase of the pretransitional divergence for Q_b

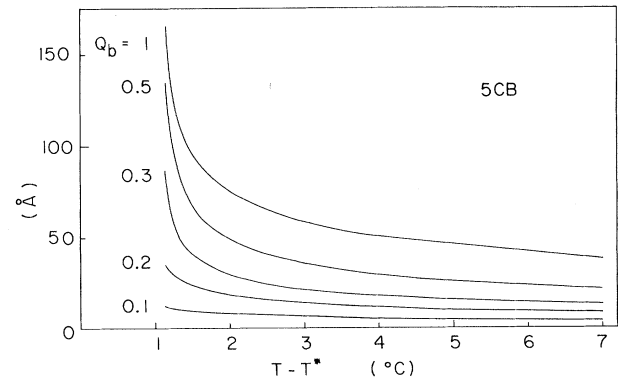


FIG. 1. Numerical calculations of $\int_0^\infty Q(z)dz$ for several boundary values, Q_b , as a function of temperature.

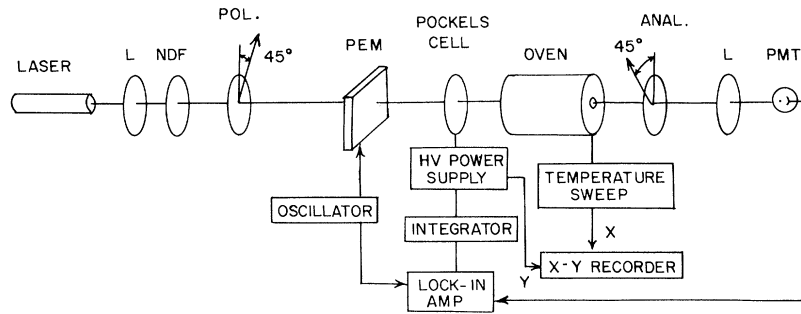


FIG. 2. Block diagram of experimental setup. L, lens; NDF, neutral density filter; and PEM, photoelastic modulator.

≥ 0.3 is due to the contribution from the region where $f(Q)$ is small and hence $Q(z)$ is relatively flat. This occurs around $Q \sim Q_c$ where Q_c is the order parameter of the nematic phase at the transition.

The birefringence was measured by the setup shown in Fig. 2. The voltage applied to a Pockels cell needed to achieve a null was recorded as a function of the sample temperature. The temperature was swept at rates between 0.1 and 0.5°C/h. The result was independent of the sweep speed in this range. The light intensity at the sample was estimated to be 0.2 μW. Although the electro-optic constants of the Pockels cell depend on the cell temperature, this did not present any problem since the applied voltage was close to zero; the noise was mainly due to the sources other than room-temperature variations. The nematic liquid crystal 5CB was chosen for its chemical stability.

Planar (director parallel to the substrate) samples were prepared between fused quartz

plates and viewed perpendicularly to the sample. Homeotropic (director normal to the substrate) samples were made between two 90° prisms whose hypotenuse surfaces were put together to form a cube of 7-mm sides and viewed at 45° as shown in the inset of Fig. 3. In both cases the substrates were lightly squeezed together by stainless steel clips without spacers. The non-flatness of the substrate surface provided the sample thickness of about 1 μm. It is important that the minimum force is applied to the substrate so that the strain-induced birefringence is as low as possible.

The homeotropic alignment was achieved with hexadecyltrimethylammonium bromide (HTAB).⁸ A typical trace is shown in Fig. 3. The least-squares fit to Eq. (4) is shown as open circles. The order parameter, Q_b , was found to be 0.32. As a result of the birefringence of the substrate, which exists in any ordinary glass and is also slightly temperature dependent, the base line of the trace had to be made adjustable. A base line

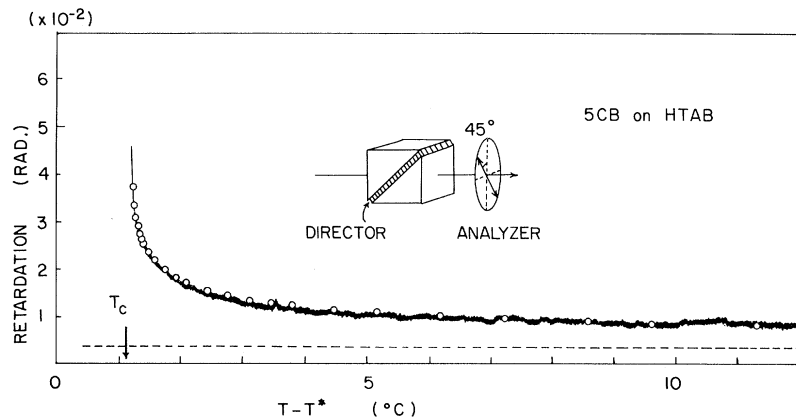


FIG. 3. Pretransitional birefringence in a homeotropic film. Inset is the experimental geometry; the director is perpendicular to the hypotenuse surfaces of two prisms.

thus determined is shown as a dashed line. The proportionality constant in Eq. (4) was calculated using an approximate form⁹ for a tilted uniaxial crystal with the assumed birefringence of $\Delta n = 0.185$ for $Q = 0.58$, which was obtained from Horn.¹⁰ The fact that there are two interfaces in a film was also taken into account. The fit is quite good. The order parameter Q_b depends on the choice of parameters, of course; if one uses $\xi_0 = 3 \text{ \AA}$ then $Q_b = 0.57$, and for $\xi_0 = 10 \text{ \AA}$, $Q_b = 0.14$.

The planar alignment was achieved by evaporating SiO or SiO₂ obliquely onto the substrate.¹¹ In contrast to the behavior of a film between HTAB surfaces, the birefringence of a 5CB film stayed constant until the temperature reached T_c , where a sudden jump occurred. This is shown in Fig. 4 in an expanded temperature scale together with the trace for homeotropic alignment for comparison. It is speculated¹² that the aligning action of an obliquely deposited film is due to the grating-like structure of the film. An energy consideration shows¹³ that such a mechanism is possible and some circumstantial evidence supports the idea. However, since 5CB tends to orient perpendicular to untreated clean fused quartz surfaces it was felt that the molecules might in fact prefer homeotropic alignment in the isotropic phase. The alignment is then forced to switch to the planar orientation in the nematic phase because of the presence of the grooves. This question was checked by the following experiment.

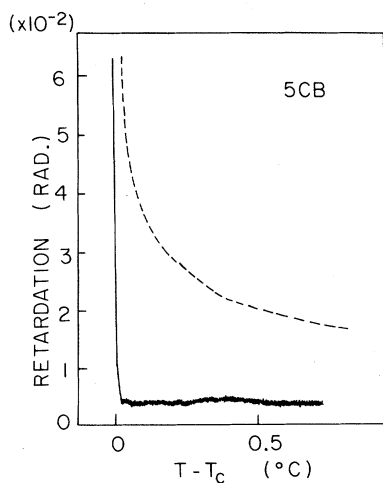


FIG. 4. Birefringence of a planar sample between SiO films near T_c . The diverging behavior of a homeotropic sample is shown in a dashed curve for comparison.

SiO was evaporated obliquely onto surfaces of 90° prisms so that, in the nematic phase, the director lies in the plane made by the analyzer axis and the light beam when the prisms are placed as shown in the inset of Fig. 3. Therefore, no net birefringence was seen in the nematic phase. However, if molecules tend to assume a homeotropic orientation in the isotropic phase, a pretransitional birefringence should be seen in this geometry just as before; no such behavior was observed. This experiment served to prove two points: (1) The molecules have little tendency, if any, to lie perpendicular to SiO film, and (2) the pretransitional behavior observed in a homeotropic film was not due to an artifact caused by a change in the averaged index of refraction in an obliquely viewed film.

It is clearly shown here that a LC can have a rather stable planar structure while it has no preferential orientation on the molecular scale. The alignment occurs only below T_c where the Frank elastic energy favors a planar orientation. In the isotropic phase, where the coherence length is less than the dimension of the grooves, the LC molecules do not feel any geometrical features of the substrate. Thus the birefringence is turned on suddenly when the long-range order appears at T_c in agreement with the observation in Fig. 4.

The orienting action caused by a surface treated by HTAB or similar chemicals is sometimes referred to as "strong anchoring." Such a description might lead to an erroneous concept that the order parameter on the wall is unity, an assumption used in model calculations.³ A high degree of ordering is rather unphysical unless there is an extraordinarily strong interaction, such as chemical binding, between the LC molecules and the wall. In this respect the observed value of $Q_b = 0.32$ seems reasonable.

Further study with different surfaces and LC's together with the details of the experiment will be given in a separate paper.

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Optically Polarized Conduction-Band Electrons in Tungsten Observed by Spin-Polarized Photoemission

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Along the (100) direction of tungsten, interband transitions induced by circularly polarized light of energy $1.5 \text{ eV} \leq h\nu \leq 4.1 \text{ eV}$ lead to spin polarization of the excited conduction electrons. This is observed by measuring the spin polarization of the photoelectrons emitted from a cesiated crystal surface. The measured polarization values depend sensitively on the s -, p -, and d -hybridization properties of the conduction bands. Excited-state lifetimes are obtained from the widths of the polarization structures.

The now widespread use of synchrotron radiation in angular resolved photoemission has made it increasingly clear that the optical selection rules for linearly polarized light provide an elegant means for identifying the parity of electronic states.¹ In this paper we show that the symmetry properties of the electronic wave functions can be investigated in further detail by photoemission using circularly polarized light. The present technique requires the measurement of the spin polarization of the photoelectrons.

The experiment is based on the fact that unpolarized electrons can be excited by circularly polarized light into spin-polarized final states. Although such optical polarization experiments have been made earlier with use of selected transitions in semiconductors,^{2,3} only the present measurements with tungsten indicate that final-state polarization can be obtained under very general conditions also for metals.⁴ Therefore it appears worthwhile to explore the possibilities of this method systematically. As it relies on the selection rules for circularly polarized light, the symmetry of the electronic states is of crucial importance. A decomposition into spin orbitals of

given l value (l is the orbital angular momentum quantum number) is useful. The symmetry properties of the spin orbitals are found from group theory. The spin polarization in each excited state is determined by the mixing of the spin-"up" and -"down" components in this state.

Essential points of the experiment are as follows: (i) The axial vector defining the direction of the final-state spin polarization is given by the spin direction of the circularly polarized light. (ii) In the absence of spin-orbit coupling the electronic wave functions are pure spin states. Then, because light interacts only with the orbital motion of the electrons, spin-up and -down electrons participate identically in all transitions and no overall spin polarization is obtained. Therefore spin mixing by spin-orbit interaction in at least one of the states involved in a given transition is necessary for final-state spin polarization. (iii) Simple symmetry considerations show that for crystals with inversion symmetry, as, e.g., tungsten, transitions produced by right- and left-circularly polarized light have the same absolute values of the polarization but opposite signs.