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REFRACTIVE INDEX MEASUREMENTS AT A 2nd ORDER SMECTIC A TO C PHASE TRANSITION

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Abstract. — A measurement of the 3 principal refractive indices of azoxy-4,4’ (di-undecyl α-methyl cinnamate) is made in the vicinity of the 2nd order smectic-A to smectic-C phase transition. The experimental procedure is : first the index differences are measured using the conoscopic method, then the absolute value of one of the indices is determined using an Abbe refractometer. In the smectic-A phase, a slow quasi-linear temperature dependence of the indices is found. In the smectic-C phase a faster effect adds to the smectic-A background. This effect is studied in more detail, and discussed in terms of angular fluctuations of the molecules.

The smectic-C liquid crystal phase is known to have monoclinic symmetry [1] i.e. to be biaxial [2, 3]; so there exist 3 principal refractive indices in the C phase. Here we present measurements of these 3 indices versus temperature in AMC-11 (azoxy-4,4’ (di-undecyl α-methylcinnamate)) through the A to C phase transition. This phase transition appears to be a good second-order one since neither differential scanning calorimeter measurements (on Perkin-Elmer DSC-2) nor precise tilt measurements [4] show any jump at the transition. This compound also has the big advantage of not degrading too much with time, because of the relative stability of the azoxy bridge. Another advantage of AMC-11 is that good homeotropic alignment can be obtained using polymerized silane coated plates [5] and this point is very important for precise optical measurements.

The refractive indices were determined by first measuring the index differences using an interferometric method — conoscopy — then measuring an absolute value of one of the indices (n_d) using an Abbe refractometer.

1. Experimental set-up and method. — 1.1 Conoscopic experiment. — The set-up is shown in figure 1 : a large-aperture microscope lens focuses a He-Ne laser beam onto the sample. This light is polarized at 45° to the yz plane. A polarizer, crossed with the incident light, causes interference between the ordinary and extraordinary rays. The interference pattern is then observed on a screen at infinity. The sample is heated in a symmetric oven with a wide aperture to allow large angle conoscopy. Nevertheless, the system is carefully insulated thermally with teflon and multiple glass windows so that the accuracy in temperature is about 2 × 10⁻² °C. The sample is prepared in the homeotropic alignment in the A phase, and then slowly cooled down to the C phase using a tilted magnetic field. In this way, it is possible to suppress the molecular tilt degeneracy and to get a good smectic-C monodomain. We may do this provided that the magnetic field is not strong enough to alter the layer direction. This fact is due to the strong anchoring at the plates and is easy to test

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in the A phase since no change is observed when the magnetic field is switched on.

1.2 Abbe refractometer. — This is a total reflection refractometer (Fig. 2). The sample is prepared homeotropically directly on the prism of the apparatus. We polarize the laser light parallel to the surface of the prism so that in the A phase the ordinary index is involved. In the C phase, with no magnetic field being applied, the sample is no longer homogeneous and the director is spread over a cone. This misalignment, in fact, is useful since it ensures statistically that $n_y$, the smallest index, is involved in some part of the sample (Fig. 2a). $n_y$ is the smallest index, and so this part of the sample will produce the first total reflected ray, i.e. the limit beam on figure 2b, which makes the measurement. Thus in the C phase, we measure $n_y$ directly.

The goniometer is previously calibrated for He-Ne laser light using various isotropic liquids (like ethanol, benzene, phenol, and pure water at various temperatures) and interpolating.

The whole system, prism and sample, is thermally regulated with a water-pumped system giving a temperature precision of 1 °C.

2. Experimental results. — 2.1 Conoscopic experiment. — Photographs of the screen with its scale, are shown on figure 3 for a 220 μm thick sample. The first photograph, in the first row, shows the interferometric pattern in the A phase. It is the classical picture for uniaxial crystals with a cross and circles. Decreasing the temperature in the presence of a 12 kG magnetic field, we get the following pictures. The tilt appears (as a translation to the left referred to the reticula), the cross splits into a hyperbola and the circles become ellipses. Tilt and splitting go on increasing as the temperature is decreased down to the crystalline phase. All these photographs are filtered from the speckle due to
the laser light simply by displacing the incident light during the exposure almost parallel to itself.

The biaxiality is measured by the angle $\Delta$ between the 2 optical axes which correspond to the vertices of the hyperbola. This angle is related to the refractive indices by the formula [6]:

$$\sin \frac{\Delta}{2} = \sqrt{\frac{n_y^{-2} - n_x^{-2}}{n_y^{-2} - n_z^{-2}}};$$

$\Delta$ being measured inside the liquid crystal, and $x, y, z$ being defined in figure 4. Various samples of thickness up to 1.1 mm have been studied. The results are collected on the plot of $\Delta$ versus the tilt angle $\theta$ (Fig. 5). We verified that the magnetic field which is necessary to orient the smectic-C has no visible influence on the result since the points are scarcely moved along the curve when a 16 kG magnetic field is applied. As we know that the temperature dependence of the tilt angle in the range around 0.1 °C below the transition is a power law with $\beta$-exponent equal to 0.4 [7], figure 5 yields the temperature dependence of the difference between the 2 smaller indices, $n_x - n_y$. Note also that the tilt angle corresponding to our precision of temperature measurement ($2 \times 10^{-2}$ °C) is 2.5° so that the first two points of figure 5 are not very reliable.

The birefringence is measured using the angular diameter of the circles. We make two justifiable approximations: first, we neglect the biaxiality and regard the ellipses as circles; second, we use the small-angle calculation for tilted uniaxial crystals [6].

The experimental results are gathered in figure 6 which shows $\Delta n = n_z - n_y$ versus the temperature.

**FIG. 3.** — Successive photographs for a 220 μ thick sample when cooling the temperature through the A-C transition. The translation referred to the reticula gives the tilt.

**FIG. 4.** — The optical axes meet the summits of the hyperbola. The angle $\Delta$ is the angle between them. The tilt angle $\theta$ is the angle made by the bisectrix of the optical axes and the perpendicular to the layers.

**FIG. 5.** — $\Delta$ angle versus tilt angle. These angles are measured inside the liquid crystal.

**FIG. 6.** — $n_z - n_y$ versus the temperature.

2.2 ABBE REFRACTOMETER. — The small index $n_y$ is measured directly this way. Figure 7 shows $n_y$ versus the temperature.

3. Discussion. — 3.1 Biaxiality. — The biaxiality measurements of figure 5 can be well fitted by the full line which goes to the origin. To first order, this corresponds to a linear law which is consistent with the symmetry rules. Making a mirror reflexion, the angles change their sign: $\theta$ becomes $-\theta$, $\Delta$
FIG. 7.— $n_y$ versus the temperature.

becomes $-A$ and so $A$ is an odd function of $\theta$. If then the transition is 2nd order, the function is continuous and to first order $A$ is proportional to $\theta$.

Using the previous formula which approximates to:

$$n_x - n_y = \Delta n \left(\frac{A}{2}\right)^2,$$

(with $\Delta n = n_x - n_y$), we deduce that the biaxiality is proportional to $\theta^2$.

This also is consistent with the symmetry rules. A scalar, or a symmetric second-rank tensor does not change in a mirror reflexion, so it is an even function of $\theta$. And because of continuity this function is proportional to $A + B\theta^2$.

Considering the temperature dependence of the tilt [7], we deduce the temperature dependence of the biaxiality:

$$n_x - n_y = 10^{-3}(T_e - T)^{0.8}.$$  

Note that this experimental law, valid in the 0.1°C range, corresponds to very small values for the biaxiality.

Three physical mechanisms can be given for the biaxiality:

1) It can be due to the anisotropy of the thermal fluctuations of the director [2]. The fluctuations inside the layers $(xz)$ appear to be nematic-like [8] and they can be seen as a layer-over-layer movement [9]. These fluctuations have a large amplitude. In contrast, the fluctuations perpendicular to the layers $(yz)$ are coupled to the dilatation of the layers, and so they are of weak amplitude. Overall the fluctuations are non-symmetrical. Since the large polarisability along the molecular axis has a greater component in the $x$-direction due to these fluctuations than in the $y$-direction, we can see that $n_x$ will be a little bigger than $n_y$.

2) The molecular environment is monoclinic [1] and the free rotation of the molecule around its long axis is biased, giving rise to biaxiality. (It is this biased rotation which allows ferroelectricity [10] for chiral molecules, when the lack of symmetry leads not only to biaxiality, but to a macroscopic permanent dipole [11].)

3) The induced dipoles in the tilted molecules do not polarize symmetrically, because of their particular arrangement in layers. This effect can create biaxiality [12].

It is possible to make an estimation of the first effect [4]; but we ignore sign and amplitude for the two others. Probably these three effects are superimposed.

Now, although these explanations are quite satisfactory, let us come back to figure 5 and look at it more carefully. Another fit not starting from the origin (broken line), seems to be better than the first one. It just avoids 6 points near the origin which correspond to bad photographs: Nevertheless we must be cautious. This small deviation can be due to systematic errors or artifacts as described in the appendix. Better experiments are under way to test these possible artifacts. If the deviation persists, we propose one of these 2 explanations as possible:

1) One of the three physical mechanisms mentioned above quickly saturates, for example the last one, and then acts as an additive constant to the polarizability difference $e_x - e_y$ and so to the biaxiality $n_x - n_y$. This gives a hyperbolic dependence of $A$ versus $\theta$ which approximates to a straight-line not starting from the origin.

2) Another possibility is that the transition is, indeed, first order. Then the C phase starts with finite values for $\theta$ and $A$ which are not related by the proportionality relation. An increase of $\theta$ then gives rise to an increase of $A$ due to the addition of a constant in $n_x - n_y$, as above. This also leads to a straight-line not starting from the origin. In fact, the A-C transition can be weakly first order. Nothing is visible yet on differential scanning calorimeter measurements or tilt measurements, as mentioned in the introduction, but it is possible that we have here a more sensitive test for the order of the transition.

3.2 Birefringence.—The birefringence measurements of figure 6 show a slow increase of $\Delta n$ of about $4 \times 10^{-4}$ oC$^{-1}$ when cooling in the A phase. In the C phase the increase of $\Delta n$ suddenly changes rate; it can be regarded as a transitional effect which superimposes on the background visible in the A phase. As we see, this increase above the background fits well with a power law of exponent equal to 0.8, as symmetry rules suggest.

We find:

$$\delta(\Delta n) = 10^{-2}(T_e - T)^{0.8}.$$  

The physical interpretation for this is the following: when the temperature is decreased, the thermal vibrations become weaker; and in particular the
orientational vibrations become weaker since the translational order should not be involved very much in the A-C transition; so the angular order parameter \( S \) increases [16]. Now, because the angular order parameter \( S \) is proportional to the birefringence [1] (approximately), it is reasonable to find an increase of birefringence when decreasing the temperature. This increase then adds to the slow increase in the A phase to give the total birefringence.

Now, if we look carefully at the transition, we remark that the birefringence decreases below the values of surrounding points in A or C phases. This can be understood as a pretransitional effect in the A phase [17]. The proximity of the C phase leads to big amplitude fluctuations of the tilt. This should cause a drop in the angular order parameter and consequently a drop in birefringence. This effect has been noted by K-C Lim and J. T. Ho [17]; although in a different compound, the measured drop in reference [17] is about 3 orders of magnitude smaller than ours. Another possible interpretation of our measurement takes note of the bad quality of the photographs related to this drop in birefringence. This suggests that the alignment of the sample at this stage is not perfect, perhaps due to small rearrangements at the transition. So the sample appears more isotropic and we measure a smaller birefringence.

3.3 \( n_y \) MEASUREMENTS. — As is seen on figure 7, \( n_y \) behaves the same way as the birefringence. First \( n_y \) decreases slowly when cooling in the A phase, with a quasi linear variation of about \( 1.5 \times 10^{-4} \)%/C [18]. Then, in the C phase \( n_y \) increases again. This change of rate could be interpreted as linear with the temperature but it is better to fit it, within uncertainties, to a power law of exponent equal to 0.8, following the symmetry rules. This effect is also very weak; it is about two orders of magnitude smaller than the birefringence change; relative to the A phase background, we have:

\[
\delta(n_y) \approx 4 \times 10^{-4}(T_e - T)^{0.8}.
\]

4. Conclusion. — We have made careful measurements of the 3 optical indices at the smectic A to C phase transition. They appear to be sensitive to the transition, but not to the same extent. The temperature variations of \( n_x \) and \( n_y \) in the A and C phases appear to be less than \( 10^{-3} \)%/C (see Table). In most applications, therefore, the \( n_x \) and \( n_y \) variations can be neglected. The optics of the smectic C phase of our compound reduces then to that of a tilted crystal with a constant ordinary optical index and an extraordinary index slowly increasing when cooling.

Physical interpretations are proposed for the temperature variations of the birefringence and the biaxiality which are based mainly on the molecular fluctuations. A statistical calculation of these fluctuations has been done and will be published elsewhere.

Some points are not clear yet and need to be studied further:

1) is the dashed fit for the biaxiality better? If so, is the transition really a second order one?
2) is the drop at \( T_c \) in the birefringence measurements a real effect?

To clarify these two difficult and important points, more precise experiments with better samples are needed.

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## APPENDIX

We present 3 proposed artifacts for the off-origin fit of \( \Delta \) angle versus tilt angle in figure 5.

1) Some systematic error can arise in when measuring \( \Delta \), especially for small values. The intensity shape of each branch of the hyperbola is symmetrical and the mid-point is rather confused with the maximum intensity-point when measuring. This could explain an increase of 1° for \( \Delta \). In reality, for thicker samples the hyperbola becomes proportionally thinner and there should be less confusion.

2) Some small \( T_c \) gradients exist and, especially for small values of \( \theta \), cause an asymmetry in the hyperbola and the rings. Thus the estimation of the centre is biased, and so \( \theta \) will be false. In reality, it is not clear why this effect should affect \( \theta \) the same way (sign and amplitude) for all our independent samples.

3) Due to the depletion of the layers when cooling down to the C phase, some undulations can appear [13]. Before vanishing, they could create small invisible edge dislocations or focal conics stuck on the glass. Provided they have a general orientation parallel to the \( x \)-direction — and this will happen if \( A(\pi/2) > A(0) \) in the notation of reference [14] —, they will cause the appearance of some pseudobiaxiality [15]. In reality, these defects are confined to the sur-
faces, and thus this structural biaxiality should be inversely proportional to the thickness of the samples. Since we do not see any thickness dependence within error bars on the measurements in figure 5, we can reasonably eliminate these 3 proposed artifacts and think of this off-origin fit as really probable.

References

[7] $\theta \approx 0.2 \Delta T^{0.4}$ in the range of 0.1 °C; see ref. [4].