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Effect of the temperature range of the nematic phase on the induction of a twist grain boundary phase in non-chiral liquid crystals

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Recent experimental results suggest that the twist grain boundary phase may be induced in non-chiral smectic liquid crystals by confining the material in a twist cell in which the nematic directors at the two surfaces are perpendicular to each other. However, the effect of the temperature range of the nematic phase on the induction of the twist grain boundary (TGB) phase has not been studied to date. We have performed experiments on non-chiral liquid crystals having the nematic–smectic A (N–SmA) phase transition sequence and confined in a twist cell. It is observed that materials with a second order N–SmA phase transition show characteristics of a TGB phase, but a material with a first order N–SmA transition does not.

1. Introduction

One of the most significant outcomes of the analogy between smectic liquid crystals and superconductors, first described by de Gennes [1], is the discovery of the liquid crystals analogue of the Abrikosov flux lattice seen in type II superconductors. Renn and Lubensky [2] theoretically predicted the existence of such a phase in chiral liquid crystals, and called this the TGB phase. Around the same time, Goodby and coworkers [3–7] reported the first experimental observation of the TGB phase, generating a great deal of interest in this research field. As a result, the TGB phase has since been observed in numerous compounds [8–13].

In the model for the structure of the TGB phase, smectic slabs of constant thickness are stacked regularly along the twist direction. Two adjacent smectic slabs are separated by a grain boundary that allows the rotation of the layer normal by a finite angle. TGB phases can either be thermodynamic phases of chiral smectics or induced by surface anchoring [14] in non-chiral materials. The latter case strongly emphasizes that chirality may not be necessary to observe the TGB structure. In fact, Patel has experimentally shown [15] that TGB structures may be obtained by confining non-chiral liquid crystals in a twist cell in which the directors at the two surfaces are perpendicular, i.e. in a cell bounded by a top surface favouring the molecular alignment along, say, the x-direction, and a bottom plate which favours molecular alignment along the orthogonal y-direction. Along the z-axis the twist is induced in the cell due to the director pinning at the two surfaces. The induced twist is detected by placing the cell between crossed polarizers and finding non-zero transmitted light intensity. Patel has detected non-zero transmitted light intensity not only in the nematic (N) phase, where it is expected, but also in the smectic A (SmA) phase. Very recently, an extensive molecular dynamics simulation study was performed by Allen *et al.* [16] in which a structure similar to the TGB phase was observed on cooling a system from the twisted nematic phase to a temperature well within the SmA phase. Moreover, TGB structures induced by strain have been observed in suspensions of the bacteriophage fd [17].

Patel has observed the TGB phase in a number of non-chiral liquid crystals having the N–SmA phase transition sequence, indicating the generality of the induction of TGB-like phases in non-chiral liquid crystals. However, the effect of the temperature range of the N phase on the observation of the TGB phase has not been investigated. In view of this, we have carried out a more systematic study on two non-chiral liquid crystals, one exhibiting a first order and the other a second order N–SmA phase transition. The results clearly indicate that the observation of the TGB phase is related to the nature of the N–SmA phase transition.

2. Experimental

The two liquid crystalline compounds chosen for this study, and their phase transition temperatures measured on cooling, are: (**A**) 4-(4-butyloxybenzoyloxy)-4′-cyanoazobenzene I 287°C N 108°C SmA 75°C Cr, and (**B**)

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4-[4-(3,7-dimethyloctyloxy)benzoyloxy]-4′-cyanoazobenzene I 215°C N 212°C SmA 65°C Cr. These materials were synthesized using standard synthetic procedures [18]. The material **B** exhibits a short nematic range which should render the N–SmA phase transition first order following McMillan's theory [19]. As expected, we found it to be first order from the DSC studies. In contrast, compound **A** has a relatively wide nematic range and consequently a small latent heat for the N–SmA phase transition.

The samples were sandwiched between two indium tin oxide (ITO) coated glass plates separated by Mylar spacers. Typically the cell thickness was of the order of 10 μm. A polyimide layer was spin coated onto the conducting surface of the glass plates and unidirectionally rubbed. The cells were assembled in such a way that the rubbing directions of the polyimide layers on the two glass plates were at 90 degrees to each other. Optical microscopic observations were performed using a polarizing microscope (Leitz DMRXP). The sample temperature was regulated using a programmable hot stage (Mettler FP90). In order to measure the twist we used a rotating analyser in which the analyser (a Glann–Thompson prism polarizer) was mounted on a rotation stage (Newport M-395CC) and rotated using a motion controller (Newport ESP6000-DCIB). The transmitted light intensity was detected by a photodetector (Hinds DET-90) and the signal was fed to a lock-in amplifier (SR 830) through a signal conditioning unit (Hinds SCU-90). The twist cell was filled with the samples in the nematic phase. Before beginning the experiment, we ascertained that in the nematic phase the sample alignment was very good and that there was a rotation of the plane of polarization of light in the nematic phase. Thus by using the polarized light and analysing the polarization state of the output light, we could establish the twist in the birefringent structure.

X-ray scattering experiments were performed using CuK_α radiation from a 1.2 kW X-ray generator (Enraf-Nonius FR 590). The scattered radiation was collected on a two-dimensional image plate director (MAC Science DIP1030). The instrumental resolution in reciprocal space was about 1×10^{-2} Å^{-1}.

3. Results and discussion

When the sample in the nematic phase was viewed between crossed polarizers, we observed a bright field of view, indicating the existence of a twist in the structure. Consequently, the plane of polarization of light is rotated through 90° because of the partial waveguiding. For compound **A** across the N–SmA phase transition the transmitted light intensity does not appear to change dramatically, suggesting that the structure remains twisted even in the SmA phase. No clear textural changes were observed across the transition. On the other hand, if the sample is placed between two parallel polarizers, the onset of the SmA phase is clearly seen with the sudden appearance of brisk director fluctuations, and the field of view slightly brightens compared with the dark field of view seen in the nematic phase. On cooling further, there is a gradual increase in the intensity of the transmitted light. By contrast, in material **B** the onset of the SmA phase is very dramatic with the appearance of bâtonets in the dark region, which grow on further cooling, resulting in a bright region. This observation clearly indicates that the structure is untwisted in the SmA phase of this compound.

We quantified these visual observations by measuring the transmitted light intensity as a function of temperature. In figure 1, we show the data for material **A** which has a wide temperature range nematic phase (~ 180°C). While the onset of the SmA phase is manifested by a slight change in the transmitted light intensity, it does not change dramatically across the N–SmA transition. This indicates that the structure in the SmA phase is similar to that of the twisted structure seen in the nematic phase. In the absence of a twisted structure in the SmA phase, the transmitted light intensity would have changed dramatically across the twisted nematic to SmA phase transition. In fact, such behaviour was observed for material **B**. It can be seen from figure 2 that the transmitted light intensity varies dramatically across the N–SmA phase transition. The dramatic change in light intensity is associated with the change in the structure from being twisted in the nematic phase to being untwisted in the SmA phase.

It can be seen from figure 1 that there is a slight increase in light intensity on decreasing temperature that may be associated with the change in birefringence of

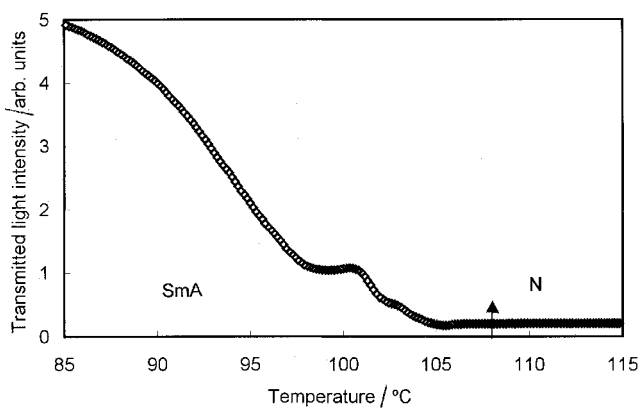

Figure 1. Transmitted light intensity plotted as a function of temperature for material **A** in a 10 μm twist cell. The arrow indicates the N–SmA phase transition temperature. The sample is between parallel polarizers and in the nematic phase the director defines a 90° twist.

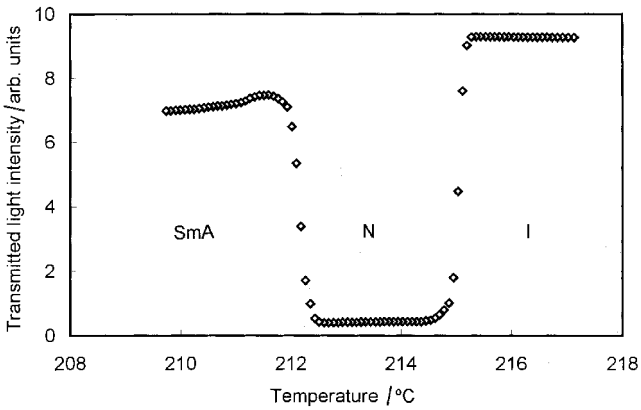

Figure 2. Plot of transmitted light intensity as a function of temperature for material **B** in a 10 μm twist cell. Sample is placed between parallel polarizers. In the nematic phase the director defines a 90° twist.

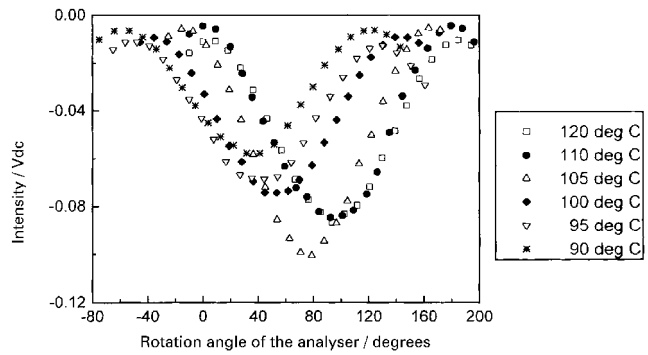

Figure 3. Plot of the transmitted light intensity as a function of the rotation angle of the analyser for material **A** in a 10 μm twist cell.

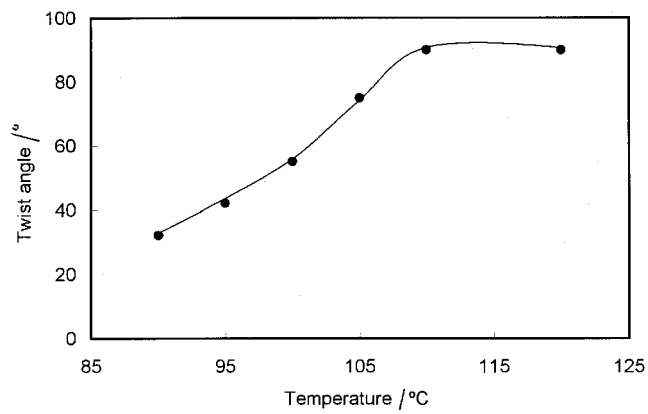

Figure 4. Plot of the twist angle as a function of temperature for material **A**. Solid line is a guide to the eye.

the sample. From careful optical microscopic observations it is seen that there is a continuous change in the colour of the birefringent sample, and at several degrees below the N–SmA transition many birefringent colours develop resulting in a patchy texture. These changes may be due to the increase in the smectic block size.

One of the most interesting features in the data presented in figure 1 is that the transmitted light intensity in the SmA phase shows several kinks in its variation with temperature. It may be recalled that in the TGB structure many smectic blocks are stacked one over the other, and the number of the smectic blocks has to be an integer. Since the number of smectic blocks changes with temperature, it is expected that the transmitted light intensity in the TGB phase should change in a stepwise fashion. It is difficult to estimate the number and size of the smectic blocks from these data. It is likely that the smectic block size may depend on temperature and at several degrees below the N–SmA phase transition, the block size may increase considerably, resulting in an increase in the intensity of the transmitted light. This should give a change in the twist angle resulting in less waveguiding.

In order to confirm this suggestion, we measured variation of the twist angle with temperature. The plot of transmitted light intensity of a He-Ne laser as a function of the rotation angle of the analyser for material **A** is shown in figure 3. It can be seen that in the N phase the intensity peaks when the polarizers are crossed. This indicates that there is a 90° twist in the birefringent structure which is nearly temperature independent. However, in the SmA phase the angle corresponding to the peak intensity is seen to vary with temperature. In fact, figure 4 shows a smooth variation of the twist in the SmA phase with temperature. However, to map out the correct profile of the twist angle variation, data measured in smaller intervals of temperature are needed in the SmA phase; such experiments are in progress. Nevertheless, the temperature dependence of the twist angle could be one of the reasons for the increase in the transmitted light intensity on decreasing the temperature. The plot of the transmitted light intensity as a function of the rotation angle of the analyser for material **B** is shown in figure 5. In the nematic phase, the maximum intensity is seen for crossed polarizers because of the twisted structure of the nematic phase. By contrast in the SmA phase, the transmitted light intensity is maximum for parallel polarizers and is nearly zero for crossed polarizers. This clearly establishes the fact that the structure is being untwisted in the SmA phase. Similar optical behaviour was seen in the experiments conducted on a number of twist cells with sample thicknesses ranging from 2.5 to 50 μm, indicating that the thickness of the sample does not alter any of the observed optical characteristics of these two materials.

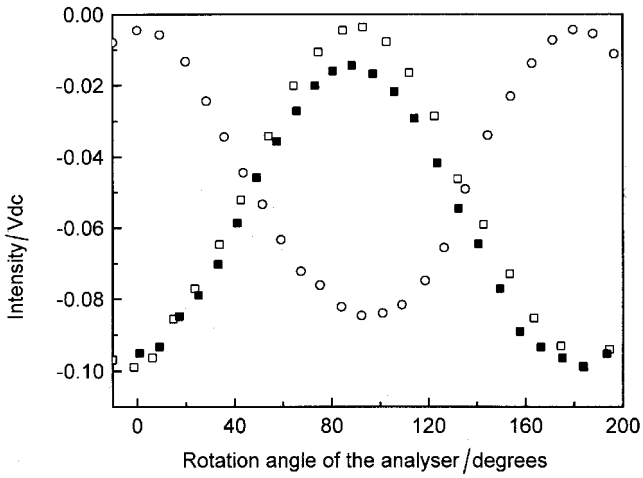

Figure 5. Plot of the transmitted light intensity for material **B** in a 10 μm twist cell as a function of the rotation angle of the analyser. □ = isotropic, ■ = smectic A, ○ = nematic.

Also, many other non-chiral liquid crystals with wide nematic ranges have shown optical behaviour similar to that of material **A**.

It should be mentioned here that it is possible that instead of grain boundaries separating the smectic blocks, nematic-like structure may separate the smectic blocks, facilitating the rotation of the blocks with respect to each other. However, it is very difficult to distinguish optically between these two possibilities. We rule out the possibility of a surface stabilized nematic texture in the SmA phase because the optical observations are reproduced in the SmA phase even on cooling from the homeotropically aligned nematic phase obtained by the application of an electric field.

It is known that X-ray diffraction experiments performed on oriented TGB phases have revealed a continuous ring whose profile is consistent with the Renn and Lubensky model. It is clear, therefore, that the X-ray diffraction patterns of materials **A** and **B** must be totally different. The twisted structure shown by material **A** in the SmA phase should clearly be seen in the X-ray diffraction pattern as a TGB structure consisting of a number of smectic blocks. Thus we performed X-ray diffraction experiments on these two materials in a twist cell. The sample was rapidly cooled from the nematic phase to a temperature 5°C below the N–SmA phase transition and then exposed to the X-ray beam which was parallel to the twist axis. The χ scan taken for material **A** is shown in figure 6. The angular variation of the integrated intensity over the scattering arc on one side of the beam stop only is shown. The complete diffracted pattern due to the low angle Bragg scattering is shown in the inset. In a TGB structure the discrete rotation of the smectic blocks can be seen in the X-ray scattering pattern. Each smectic block results in two

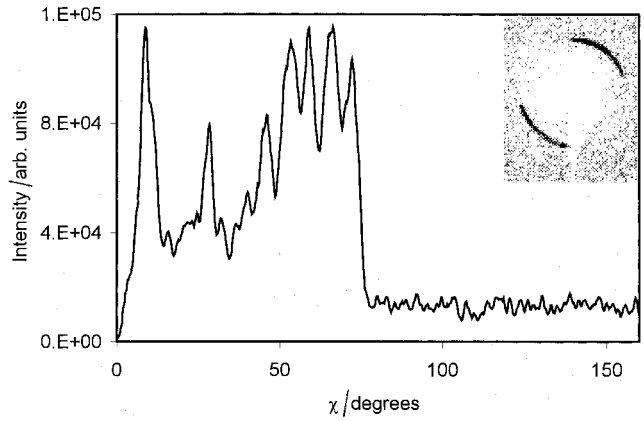

Figure 6. Angular variation of the intensity over the scattering are on one side of the beam stop for material **A**. The sample is taken in a twist cell of 50 μm thickness and at a temperature 5°C below the N–SmA phase transition. The scattered intensity is integrated over the Bragg scattering ring centred around $q = 0.268$ Å^{-1}. A two-dimensional intensity map recorded in a plane perpendicular to the pitch axis is shown in the inset. The intensity spread is seen from 0° to 80° and from 180° to 260° on either side of the beam stop.

symmetrical spots. As a result, the scattering pattern of the TGB phase will have a number of spots; each spot is due to a block. It is evident from the χ scan that there are many spots in the arc spreading over 80 degrees as many maxima and minima are seen in the integrated intensity profile. It should be noted here that the pattern was obtained in many experiments and for various thicknesses of the sample, indicating that the observed pattern may not be due to the mosaicity of the sample. The χ scan taken for material **B** is shown in figure 7. The intensity spread seen in this case is due to the existence of two domains in the sample. These results

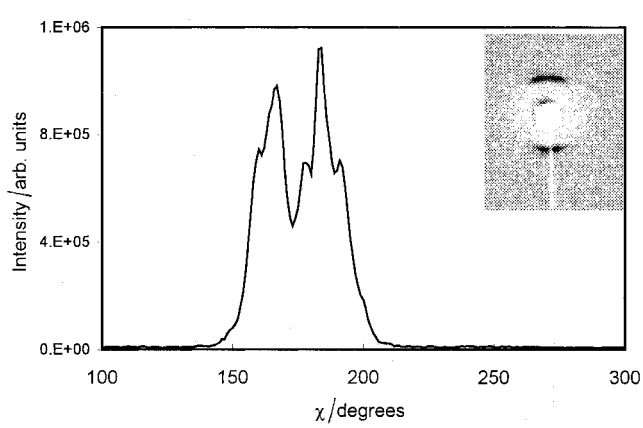

Figure 7. Plot of the scattered intensity as a function of the angular coordinate on one side of the beam stop for material **B**. The sample is taken in a twist cell of 50 μm thickness. A two-dimensional intensity map recorded in a plane perpendicular to the pitch axis is shown in the inset.

are in accord with our optical observations that the SmA phase of material **A** shows evidence of a TGB-like structure while material **B** does not show a TGB structure.

It is interesting to note that the SmA phase of the material exhibiting a first order N–SmA phase transition does not show the TGB phase, while the SmA phase of the material exhibiting a second order N–SmA phase transition does exhibit the TGB phase. This is a noteworthy result for it clearly proves the existence of a lose relationship between the observation of the TGB structure in a non-chiral system with the temperature range of the N phase.

In conclusion, the optical observations along with supporting X-ray results appear to indicate a close relationship between the observation of a TGB-like structure and the nature of the N–SmA phase transition. However, many more experiments are now needed in order to obtain a better understanding of the phenomenon.

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