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Dynamics of the modulated crystal smectic B phase of 50.7 by neutron scattering experiments

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Résumé. — La nature coopérative du mouvement moléculaire dans les phases smectique B et smectique G du 50.7 a été étudiée par diffusion cohérente de neutrons sur un échantillon complètement deutéré. On en a conclu que la modulation transverse incommensurable de la couche smectique B, qui croît lorsqu'on approche de la phase smectique G, est une déformation statique des couches. Dans le spectre d'énergie de nouvelles excitations doivent donc être associées à la modulation des couches. On discute les raisons pour lesquelles de telles excitations n'avaient pas été observées.

Abstract. — The cooperative nature of the molecular motions in the crystal smectic B and smectic G phases of 50.7 have been investigated using coherent neutron scattering from a fully deuterated sample. It is concluded that the incommensurable transverse modulation of the smectic B layers, which develops as the smectic G phase is approached, is a static deformation of the layers. New excitations in the energy spectrum should therefore be associated with the layer modulation. Reasons why such excitations were not observed are discussed.

1. Introduction.

The N-(4-n alkoxybenzylidene)-4′ alkylanilines (CₐH₂ₐ₊₁ 0 PhCHNPhCₐH₂ₐ₊₁ ; n=0,m) have a rich smectic polymorphism which has been studied by X ray and neutron diffraction [1]. Several members of the series exhibit a crystal smectic B (SB) to smectic G (SG) transition which is preceded, in cooling through the SB phase, by a strong transverse modulation of the smectic layers. A quantitative X ray diffraction study of this transition [2] and a study of the diffusive molecular motions in SB and SG phases using incoherent quasi-elastic neutron scattering [1, 3] have been carried out for 50.7.

The phase behaviour of 50.7 is as follows

Crystal 15X Sₐ 35X Sₕ 55X S₂ 54X S₂ Cₜ 55X Sₐ 55X Sₐ N 28X Isotropic liquid.

The incoherent quasielastic neutron scattering measurements showed that the molecules in the SB phase reorientate about their long molecular axes with a rotational diffusion constant \( D_r = 1.8 \times 10^9 \) rad² s⁻¹. This motion is probably hindered by a weak (\( \sim k_B T \)) six-fold potential consistent with the hexagonal symmetry of the layers. In the SG phase the rotational diffusion was only marginally slower (\( D_r = 1.7 \times 10^{11} \) rad² s⁻¹) but the elastic incoherent structure factor revealed a greater degree of localization of the molecules consistent with an orientational ordering about the long axes with two preferred sites separated by \( \pi \). The orientational order parameter \( \langle \cos 2 \phi \rangle \) was estimated to be 0.9. In addition, a localized diffusive motion parallel to the long molecular axes was seen in both phases. The time averaged distribution function for the motion could be described as a Gaussian with
$\langle Z^2 \rangle^{1/2} = 1.4 \text{ Å for } S_B \text{ and } 1.1 \text{ Å for } S_G$. Correlation times for the motion were indistinguishable from those for the uniaxial rotation ($\sim 5 \times 10^{-11}$ s).

What has not been established for the $S_B$ or $S_G$ phases of 50.7 (or for other nO.m compounds) is the local correlation in orientation about the long molecular axes or the dynamics of the cooperative reorientations. One of the objects of the present work was to investigate these effects.

Figure 1 shows the neutron diffraction pattern around the 001 reflection for the $S_B$ and $S_G$ phases for a fibre-aligned specimen. The satellites reveal the presence of transverse modulations of $78 \pm 3$ Å wavelength which is about 17 times the lattice parameter but the accuracy was insufficient to determine whether or not the modulation is commensurable with the lattice. The quantitative analysis of satellite intensities [2] showed the maximum amplitude of the modulations to be $\sim 4$ Å and a motion of this amplitude was clearly not seen by the incoherent neutron scattering experiments. Coherent inelastic neutron scattering measurements on fully deuteriated specimens were therefore used to search for cooperative dynamic effects associated with the modulations and three possibilities were envisaged.

1) The modulations are static and new excitation branches are associated with the satellite reciprocal lattice points. If the modulations are incommensurable these will be phase and amplitude fluctuations (phasons and amplitudons) [4].

2) The modulations are large amplitude underdamped transverse vibrations propagating along the layers. The coherent scattering spectrum, if of high enough resolution, will show inelastic peaks with intensity proportional to $(Q \cdot A)^2$ where $A$ is the vibrational amplitude.

3) The modulations comprise an overdamped non-propagating wave whose mean lifetime would be observed as an energy broadening of the coherent scattering signal at scattering vectors at and near the satellite wave-vectors.

The second object of this work was therefore to measure the coherent scattering with high energy resolution in the vicinity of the satellite reflections to investigate the dynamical nature of the modulation.

For both objectives a fully deuterated specimen was required. This was prepared and measurements were made both on it and on a hydrogenous sample.

2. Experimental results.

About 2 g of fully deuterated 50.7 was prepared as described in the appendix. The sample was contained in a slab shaped aluminium can and fibre aligned ($c$ axes and molecular long axes parallel) by slow cooling from the nematic phase in an IT magnetic field. This alignment was maintained on going through the $S_B/S_G$ transition in either direction even though the layers tilt and a rocking curve on the 002 reflection indicated a mosaic spread of $\pm 7^\circ$.

2.1 COOPERATIVE ORIENTATIONS ABOUT THE LONG AXES. — Measurements were made on fibre aligned specimens of both perdeuteriated and hydrogenous fibre-aligned samples using the IN6 time-of-flight spectrometer [5] with energy resolution $\sim 50$ µeV (HWHM). The energy profiles of the scattering were very similar for deuteriated and hydrogenous specimens. The data could be fitted to an « elastic » plus a broad quasi-elastic component with an energy width corresponding to a relaxation time of $\sim 3 \times 10^{-12}$ s. This is much faster than the single molecule long axis rotation correlation times ($\sim 5 \times 10^{-11}$) established in higher resolution experiments [1], and by analogy with the much more extensive work on IBPBAC [6] the faster motions are suggested to be soft acoustic and internal modes. Analysis of the intensity of the elastic and quasielastic components gives root mean square amplitudes for these modes of 0.8 Å in the SB phase and 0.7 Å in the SG, and these values are to a first approximation isotropic.

The elastic scattering intensities in the $S_B$ and $S_G$ phases for scattering vectors perpendicular to the crystal $c$ axes (also the long molecular axes) are shown in figure 2. The weak peak in the diffuse scattering centred near $Q = 1.9$ Å$^{-1}$, and more well defined for the $S_G$ phase, shows that the molecules have a local ordering about their long axes which removes the C-centring of the average structures; this is probably a herringbone type of packing [7]. These experiments could not give any information about the dynamics of the cooperative rotations because the life time of the local-ordering must be at least as long as the single molecule relaxation times ($\sim 5 \times 10^{-11}$ s) and the...
Fig. 2. — The « elastic » intensity obtained from IN6 spectra. The 50.7 was in the SB (40 °C) and SG (31 °C) phases. The scattering vector, $Q$, is perpendicular to the c axis (the fibre axis) and the significance of the weak peak at $Q = 1.9 \text{ Å}^{-1}$ is discussed in the text.

The present experimental resolution was not high enough to probe this region.

2.2 Dynamics associated with the modulations. —

Three neutron scattering experiments were performed on fibre aligned specimens. In the first the spin echo spectrometer IN11 [8] was used to search for inelasticity in the scattering at the satellite wave vector (point B in Fig. 1) on a perdeuterated sample. The Bragg reflection in the SB phase (point A Fig. 1) was used to calibrate the instrument for purely elastic scattering. The sample and detector angles were then adjusted to look at the point B and the measurements were repeated with the sample 1 °C and 4 °C above the onset of the SG phase. The background was measured at point A in the SG phase. The satellite scattering was clearly observed but there was no detectable inelasticity. The instrument had an effective energy transfer resolution of $\sim 10$ meV so this result implied that a relaxation time for the structure must be longer than $10^{-7}$ s.

The second experiment was done using the IN5 spectrometer [5] which has poorer energy resolution (12 μeV FWHM with an incident wavelength of 12 Å) but its large number of detectors allowed the scattering at a grid of points around the 001 reflection to be energy analysed. Measurements were made in the SB phase and at temperatures 1 °C and 5 °C above the transition. Some of the detectors did show some quasi elastic scattering under elastic peak and the two components were separated using the program W8 [9]. However comparison with the results from a hydrogenous sample at the same detector positions and temperatures indicated that the magnitude of the quasi-elastic component is consistent with the incoherent cross section of deuteriated 50.7. The intensity of the elastic component was very large in the region of the 001 peak in the SB phase but there was no sign of it being broadened nor of any side peak and so any cooperative molecular motion associated with the satellite peaks must have a correlation time (or period) of at least $10^{-10}$ s and no information was obtained about any excitation associated with the satellite peaks.

The components of the scattering vector parallel and perpendicular to the 001 axis were calculated for each detector and the grid they form in reciprocal space is shown in figure 3. The intensity of the elastic component has been indicated by contours in figure 3 and they confirm that the sample was well aligned.

Fig. 3. — The « elastic » intensity obtained from IN5 spectra. The 50.7 was in the SB (40 °C), SG (28 °C) and at the transition (36 °C). The intensities were given as spot heights as a function of $Q_{\perp}$ (along the fibre axis) and $Q_{\parallel}$ (perpendicular to it) around the 001 reflection. Comparison with figure 1 confirms that the sample was well aligned.

A similar survey of the scattering around the 002 reflection was made in a third experiment in the SB phase using the high resolution triple axis spectrometer IN12 (with incident wavelength 5 Å and energy resolution 50 eV FWHM). This gave similar, negative, results about the presence of inelasticity at, or near, the satellite peaks.

3. Discussion and conclusion.

The coherent neutron scattering experiments described above have shown that any relaxation time associated with the modulations of the SB phase must be at
least $10^{-7}$ s. Even though the experiments were performed on fibre aligned samples rather than single crystals, it is very unlikely that the scattering from a $\sim 4$ Å motion could be missed if it were rapid enough for the energy resolution used because the scattering vector makes a fairly small angle with the molecular displacement associated with the transverse modulation. Since the transverse modulation of the $S_6$ phase involves a maximum longitudinal displacement of 1.4 Å between adjacent molecules and individual molecules can traverse this distance in $5 \times 10^{-11}$ s [11], then, if the modulation were dynamic, we might expect its relaxation time to be of a similar order of magnitude. However these experiments have shown it to be longer than $10^{-7}$ s so it seems reasonable to regard the transverse wave as a static modulation of the $S_6$ layers which are defined by the mean positions of the molecules. Such a static modulation should be associated with new excitation branches in the energy spectrum but no scattering assignable to any such excitations could be identified. For further progress in this direction a single crystal rather than a fibre-aligned specimen should be used. Similarly, for a determination of the cooperative dynamics of rotation about the long axes higher resolution experiments, again with a single-domain perdeuterated sample will be required.

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**Appendix.** — *Preparation of 4-C$_7$H$_{15}$OC$_6$H$_4$CD-N. C$_7$H$_{15}$C$_6$H$_4$CD-N.*

Perdeuterio-$d_{38}$ 4-n-pentyloxybenzyldiene-4'-n-heptylaniline was prepared from the deuterated starting materials purchased from Merck, Sharp and Dohme, Canada. The methods employed were fairly standard procedures, but in view of the high cost element, each step was carefully monitored several times using hydrogenous materials, to establish conditions that would give optimal yield and purity.

Perdeuterio-1-bromohexane was converted into the Grignard reagent which was treated with solid carbon dioxide to obtain the heptanoic acid. Thionyl chloride was used to obtain the heptanoyl chloride which was used to acylate perdeuterio-benzene in a Friedel-Crafts reaction. Reduction using LiAlD$_4$/AlCl$_3$/CDCl$_3$/Et$_2$O gave perdeuterio-heptylbenzene which in a further Friedel-Crafts reaction in dichloromethane yielded $p$-C$_7$H$_{15}$C$_6$H$_4$COCH$_3$. This was converted into the oxime which was used in the following steps:

\[
\begin{align*}
\text{C}_7\text{D}_{15} & \xrightarrow{\text{NOH}} \text{C}_7\text{D}_{15} & \text{CH}_3 \\
& \xrightarrow{\text{NaH}} \text{C}_7\text{D}_{15} & \text{NOSO}_2 \text{tosyl} \\
& \text{C}_7\text{D}_{15} & \text{CH}_3 \\
& \xrightarrow{\text{DCl/D}_2\text{O}} \text{N}(\text{Et}_3/\text{D}_2\text{O/ EtOD/heat}) & \text{C}_7\text{D}_{15} & \text{ND}_2 \text{COCH}_3
\end{align*}
\]

The oximino-tosylate was not isolated in the above procedure.

Perdeuterio-4-hydroxybenzaldehyde was alkylated with perdeuterio-1-bromopentane by a standard procedure using anhydrous potassium carbonate and propanone.

The perdeuterio-4-n-heptylaniline (1.1 mol) and the perdeuterio-4-n-pentyloxybenzaldehyde (1 mol) were interacted in dry petroleum ether (b.p. 40-60 °C) for 3 h at room temperature. The required Schiff's base was obtained in 90% yield by filtration and thrice crystallized at about 0 °C from EtOD. The product was analytically pure, and n.m.r. spectroscopy could detect no protons in the sample. The deuterium content is taken to be $\geq 99.9\%$.

Starting with 5 g of C$_6$D$_{13}$Br, 1.7 g of perdeuterio-4-n-heptanaldehyde were obtained. This amine was condensed with 1.5 g of the perdeuterio-aldehyde to yield, after final crystallization, 2 g of the pure perdeuterio-Schiff's base.

The smectic-smectic transition temperatures of the hydrogenous and deuterated samples agreed to within one degree.
References


