Experimental report :

"Extension of the resonant scattering technique to liquid crystalline materials without resonant element"

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*** ESRF, BM32**

1- Line up of the diffractometer :

The standard diffractometer GMT was used equipped with two cradles BG1 and BG2 (three-circle geometry). The liquid crystal (LC) sample was a free standing smectic film mounted in a two-stage oven (10 mK resolution) flushed with helium. The size of the LC film was 25 x 5 mm^2.

The direct beam was slitted to : 50 µm x 300 µm. (angular resolution = 0.037 deg).

The energy was set to = 12.661 keV (Selenium K-edge measured in an absorption energy scan through the LC sample).

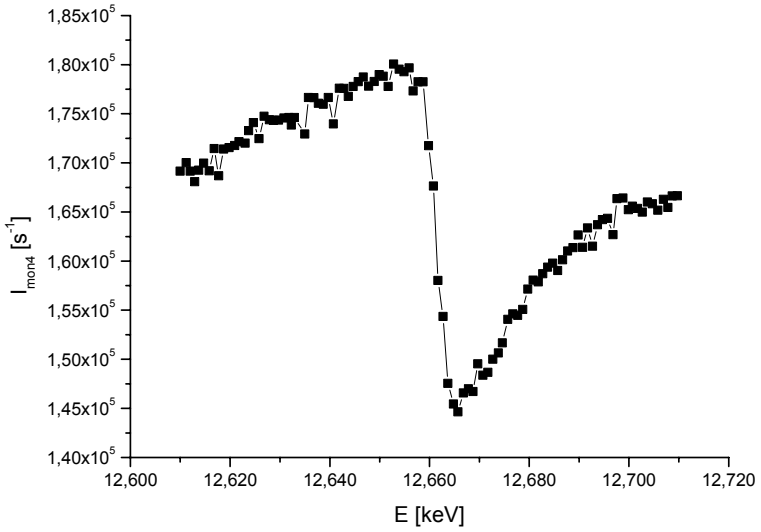

Figure 1 *- Absorption energy scan.*

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2- Experiments : MHPOBC + 5% PB237

- Film # 1:

The LC sample used was a mixture of the reference material (MHPOBC) with the selenium dopant (5% in mol). The film was drawn to a 3 mm width (3 x 25 mm).

A resonant scattering signal was observed with a reasonable intensity at half order position in the SmCA phase as expected. This observation demonstrates the potential validity of the technique. Subsequent scans on this first film were devoted to improving the quality of the alignment of the film and of the resolution of the set up. It was found that limiting the width of the film to 3 mm is not optimal for the alignment of the film (controlled by rocking scans). Opening the frame to its maximum size of 5 mm stretches the film more which improves considerably the quality of its alignment.

- Film #2:

A fresh film was drawn with a larger width (5 mm) with the same LC mixture.

Resonant peaks were detected in three phases :

- in the SmCA, quite sharp and intense resonant doublets were observed at half-order position. The splitting of the doublet is due to the long pitch helical precession of the two-layer structure. We checked that the doublets disappear upon shifting the energy by only 5 eV. (figure 2)

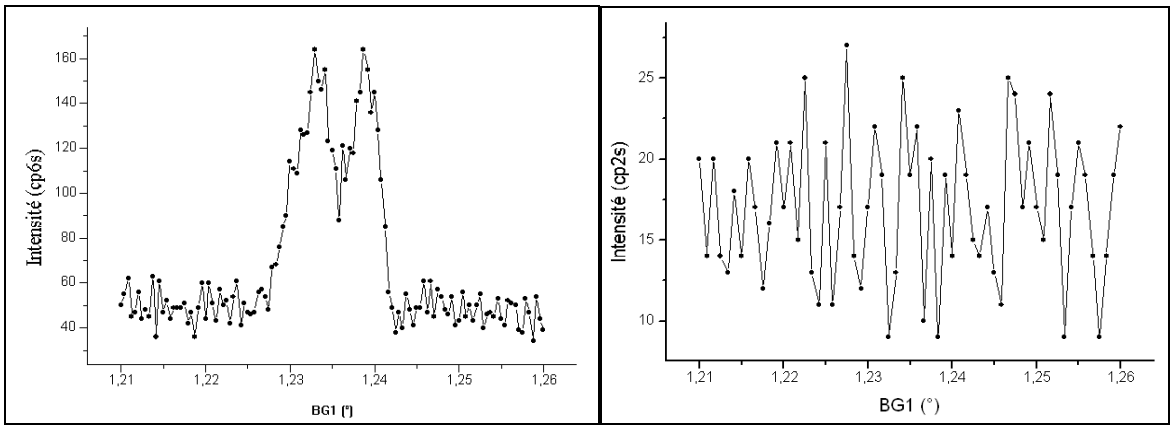

***Figure 2** – 3/2 order peak for the MHPOBC + 5% PB237 at T = 99.84°C.*
Left : E = 12.660 KeV ; Right : E = 12.650 KeV

- in the SmC_{ferri2} phase, beautiful sharp resonant peaks were observed at quarter-order position (figure 3). The half-order harmonics were also detected. These observations demonstrate for the first time the 4 layer structure of the SmC_{ferri2} phase of MHPOBC. No

internal structure was found in the ¼ order peaks upon improving the resolution (a splitting of these peaks due to the distortion of the four-layer structure was observed in other material). This last observation suggests that the microscopic structure is close to the simple clock-model. The resonant nature of the peaks was again checked by shifting the energy.

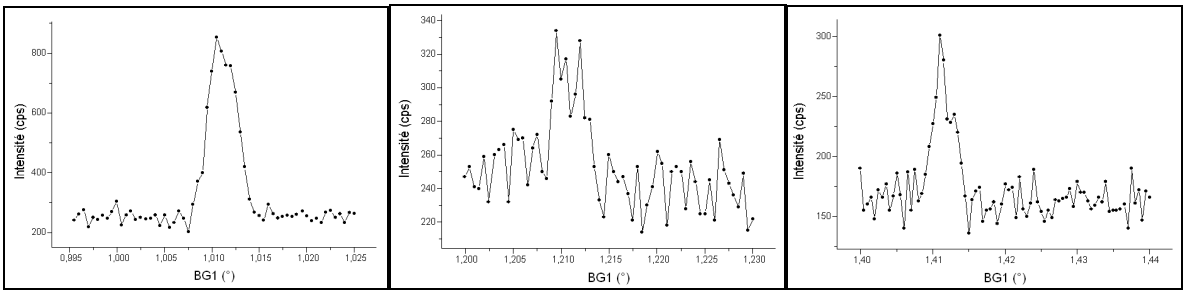

Figure 3 *– Scans for the MHPOBC + 5% PB237 at T=115.94°C and E=12.660 KeV. Left : 5/4 order peak ; Middle : 6/4 order peak ; Right : 7/4 order peak*

- in the SmC_{ferri1} phase, a set of peaks was detected at third-order positions, hence revealing the three-layer superstructure (figure 4). Like in previous experiments, the line shape of the 1/3 order features is not as sharp and as well defined as in the 4-layer phase. To our big surprise, these peaks remained present after a considerable shift of the energy (more than 30 eV). The existence of such non-resonant peaks at 1/3 order position had never been observed before (although predicted by some theories – but not all). We checked that these peaks disappear in both neighbouring phases (above and below) and reappear in the SmC_{ferri1} phase.

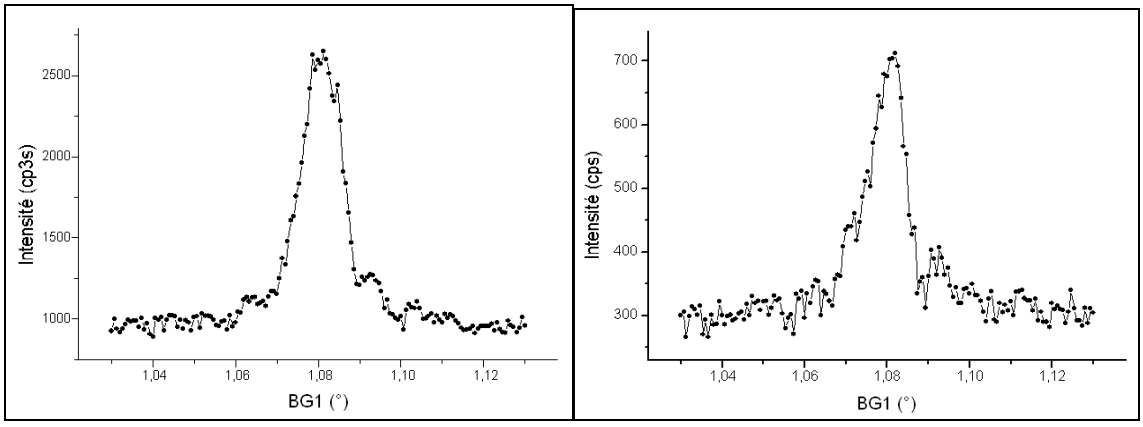

Figure 4 *– 4/3 order peak for the MHPOBC + 5% PB237 at T=115.19°. Left : E = 12.660 KeV ; Right : E = 12.680 KeV*

We did not have time however to confirm their existence on a fresh film (which should undeniably be done, given the importance of the observation).

3- Experiments : MHPOBC + 5% S2 (brominated dopant) :

The K-edge of bromine in the pure brominated material was first determined. The resonant energy was set to 13.477 keV.

Although an excellent film was drawn with the LC material, no resonant peak was found at any temperature throughout the phase sequence. The variation of the layer spacing of the smectic phase with temperature was carefully recorded in order to pinpoint the SmA-SmC transition as a reference temperature. This provided a good identification of the SmCA phase, but did not help in detecting resonant signal.

We thus came to the conclusion that the resonant signal is definitely too weak with brominated liquid crystals.

4- Conclusion:

The results obtained with the selenophene dopant are extremely important for three reasons :

- 1 – The characterization of the structure of a chiral liquid crystal by addition of a small fraction of a rod-like molecule containing the resonant element works well. The resonant signal is strong enough to provide good quality data. This observation extends the resonant scattering technique to most liquid crystals, as expected from this run.

- 2 – The structure of the two Smectic C_{ferri} phases of the reference LC material (MHPOBC) has been demonstrated for the first time.

- 3 – A non-resonant component has been found for the first time in the ferri 1 phase in 1/3 order position. This observation contradicts all previously reported resonant scattering experiments on this phase on other materials (with Se and S resonant element) but is supported by some recent theories. The observation of a non-resonant Bragg peak reveals the existence of a three-layer modulation of the electron density. Whether this unexpected modulation is present in the pure MHPOBC phase or corresponds to a modulation of the concentration of the dopant is unknown.

Given the importance of this point, it is essential to confirm the observation of the three-layer non-resonant signal in another series of experiment and to investigate the dependence of the signal on the fraction of dopant.