



Experiment title: *Research of higher harmonics Bragg peaks on alcohols monolayers of chain lengths > C12 by grazing incidence diffraction.*

**Experiment number:**  
**SC-442**

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**Report:**

The aim of this experiment was to demonstrate the feasibility of recording the Bragg peaks of higher order ( $\langle 11 \rangle$  or  $\langle 20 \rangle$ ) associated to a 2D hexagonal crystal of 1-hexadecanol. In precedent experiments realized at ESRF in July 95 and February 1996 (SC-176), we have established the scenario of melting of the 1-decanol and the 1-dodecanol [1,2]. However neither with decanol nor with dodecanol, we could observe Bragg peaks of higher order [2,4].

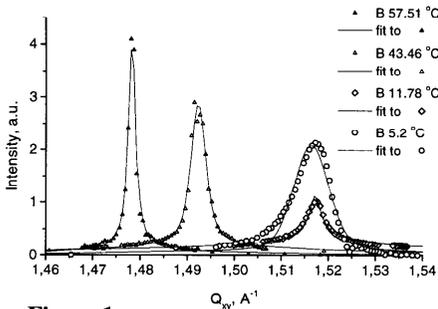
We have determined that the Bragg peak  $\langle 10 \rangle$  is a power law singularity, with  $S(Q) \propto |Q - Q_0|^{-2+\eta}$  (1), where  $Q$  is the momentum transfer and  $Q_0$  is the Bragg position. In the framework of the bidimensional melting theory, it is found  $\eta \propto TQ_0^2/h$  (2), where  $h$  is the chain length. After 2D powder averaging, the relation (1) leads to an intensity of the Bragg peak proportional to  $|Q - Q_0|^{-1+\eta}$ ; then  $\eta=1$  is an upper limit above which no other peak can be observed. Far from melting, we obtain a value of  $\eta > 0.31$  for decanol and  $\cong 0.24$  for dodecanol, for the  $\langle 10 \rangle$  reflection. This implies for decanol a value of  $\eta > 1$  for the nearest peak, associated to the  $\langle 1 \rangle$  reflection then impossible to detect. For hexadecanol the expected value of  $\eta$  is  $< 1$ , which means a detectable intensity at least of the  $\langle 11 \rangle$  reflection. In 2D systems, the bidimensional fluctuations lead to strong decrease of the X-ray scattering intensity with  $Q$ . But according to equation (2), the longer the chain is, the more rigid is the monolayer which implies that the fluctuations are less important. Therefore the Bragg peaks of higher order are more likely to be observed with alcohol monolayers of chain length  $> C13$ . All of these explain difficulties of the experiment and demand of high flux of the X-ray beam.

We have used a high resolution set-up of X-ray grazing incidence diffraction to measure the Bragg peak of alcohol monolayer. The incident beam was shaped at  $\lambda = 1.40873 \text{ \AA}$  by a Si(111) monochromator, followed by a flat mirror. The incident angle on the water surface was 2.03 mrad ( $0.8 \theta_c$ ). The sample was inside our specially designed trough having a good thermal stability and homogeneity and water level regulation better than  $\pm 5 \mu\text{m}$ . We analysed the diffracted intensity with an Ge(111) analyzer (resolution 0.011") and a vertical PSD.

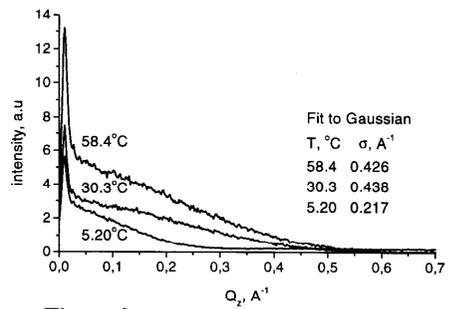
The experiment began with the installation of our home-made trough. The trough was flowed with He to reduce background. We tune and test of all the setup with reflection  $\langle 10 \rangle$  from well studied 2D crystal of 1-dodecanol. The monolayers of 1-hexadecanol were deposited in their liquid phase ( $T_{2D}$  melting is  $67^\circ\text{C}$ ) then the temperature was decreased until  $30^\circ\text{C}$ . We recorded spectra around position of Bragg peaks  $\langle 10 \rangle$ ,  $\langle 11 \rangle$ ,  $\langle 20 \rangle$  during the increasing temperature (from  $30^\circ\text{C}$  to  $67^\circ\text{C}$ ) until the melting of the monolayer and decreasing of temperature (from  $12^\circ\text{C}$  to  $5^\circ\text{C}$ ).

Some of the spectra for Bragg peaks  $\langle 10 \rangle$  are shown on Figure 1. We found that in case of hexadecanol broadening of the peak has opposite from short alcohols (decanol, dodecanol) behavior. With decreasing the temperature from the melting point ( $67^\circ\text{C}$ ) to  $5^\circ\text{C}$ , the Bragg peak for short alcohols becomes weaker and broader whereas for hexadecanol it becomes stronger and thinner. This difference could come from the increase of interaction between chains with increasing of alcohol length that leads to slight distortion of hexagonal cell with decrease of temperature. Analysis of the Bragg peak shape using power law gives that coherence length vary from  $14300 \text{ \AA}$  at  $57.5^\circ\text{C}$  to  $750 \text{ \AA}$  at  $5.2^\circ\text{C}$ .

Rodscans of  $\langle 10 \rangle$  Bragg peak (Figure 2) show that thickness of the monolayer is almost the same in wide range of temperatures ( $30^\circ\text{C} < T < 60^\circ\text{C}$ ) but is twice thick at  $5.2^\circ\text{C}$ .

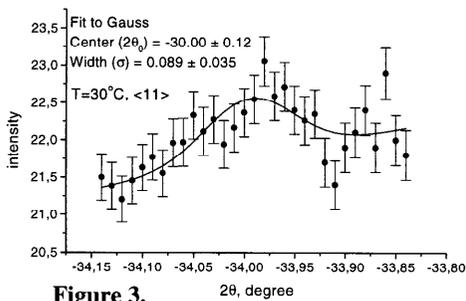


**Figure 1.**



**Figure 2.**

At each temperature we systematically tried to find Bragg peaks of higher orders:  $\langle 11 \rangle$ ,  $\langle 20 \rangle$  and corresponding to  $\langle 1/20 \rangle$ . We expect to have very weak and broad peak so we made wide range of scan in 2 $\theta$ . In all cases for peaks  $\langle 20 \rangle$  and  $\langle 1/20 \rangle$  we saw only background that linearly increase with decreasing of  $2\theta$ . Calculation of parameter  $\eta$  for peak  $\langle 10 \rangle$  carried out after the experiment gives  $\eta > 0.4$  for  $T < 30^\circ\text{C}$ . So it is not surprising that we did not observe higher orders of Bragg peak. But for  $T > 30^\circ\text{C}$   $\eta$  is less than 0.4 and we could detect at least  $\langle 11 \rangle$ . Indeed at  $T = 30^\circ\text{C}$  and  $53.2^\circ\text{C}$  we got the spectra (Figure 3) that could be interpreted as  $\langle 11 \rangle$  Bragg peak. But these spectra were not completely reproducible and on rodscans we did not see clear Vineyard peak that could be also very weak due to large width of the peak. So we are not completely sure that observed peaks are higher order Bragg peaks. Obviously that intensity of the peak is very weak and could be smeared out with diffuse scattering from the water if the position of monolayer is not at the optimum. The latter may be one of the reasons of non-reproducibility of the spectra.



**Figure 3.**

