ESRF	**Experiment title:** Pressure dependent filling of the cages in methane clathrate hydrate	**Experiment number:** HS 393
Beamline: ID15 A	**Date of experiment:** from: 19.09.97 to: 26.09.97	**Date of report:** 28.4.98
Shifts: 15	**Local contact(s):** V. Honkimäki	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

B. Chazallon* MKI, Universität Göttingen and LPCML Lyon
A. Klapproth* MKI, Universität Göttingen
E. Hensel* MKI, Universität Göttingen
W.F. Kuhs* MKI, Universität Göttingen

Report:

Samples of methane clathrate hydrate were prepared at MKI Gottingen and transported cold and under the formation pressure in Al pressure cells to ESRF. Samples were prepared using H_2O at pressures of 25,35,60, 140, 500 and 1000 bar as well as one sample using D_2O prepared at 35 bar. As the experiment was the first powder diffraction experiment for Rietveld structure refinements on this beam line, the set-up took approximately half of the shifts allocated. The set-up is shown in Fig. 1, Additional time was lost due to temperature controller problems (running the orange cryostat). For the data collection only the last few shifts could be used. It was found that some powder statistics problems existed, which made a sample rotation essential. A sample rotation scan is shown in Fig.2 exhibiting the typical variation of scattered intensity versus rotation angle. Assuming a uniform spherical size of the grains we would expect to see such intensity variations for sizes exceeding 20-30 microns. The grain size of the clathrate crystals measured with replica techniques shortly after the synthesis gave a grain size of 15-20 micron, which indicates that some recrystallization had taken place in the days between the formation and the experiment. Unfortunately it was not possible to turn the sample (i.e. the cryostat) by more than a few degrees, thus leaving some doubts on the quality of the intensity data.

As there was no software for data reduction and averaging a suite of programs was written in Gottingen to obtain a powder diffraction pattern suitable for Rietveld refinements. The refinements were performed using GSAS. They clearly indicate that the determined filling do not reach the l-2 % accuracy aimed for most likely due to insufficient powder statistics as indicated' above. A typical example is shown in Fig.3.. It should be pointed out that a data set of the D_2O 35 bar sample was also obtained with neutrons on

D2B at ILL. The refinement of this neutron data set proceeded without any problem, however the precision on the filling is insufficient to decide between competing theoretical models. The precision of the filling obtained from the ID 15A data is - despite the low quality of the fit - at least twice as good, yet the accuracy is not much improved. We have all indications that given a better powder averaging we should obtain the information wanted from high energy X-ray powder diffraction.

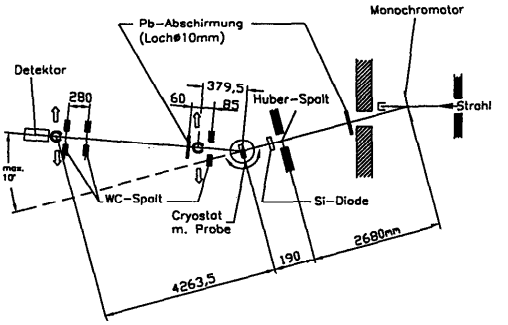

Fig.1. Experimental set-up for the high energy powder diffraction experiment

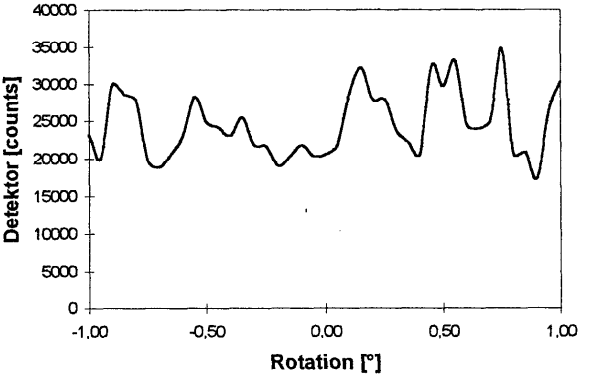

Fig.2 Intensity of a main clathrate reflection vs. sample rotation

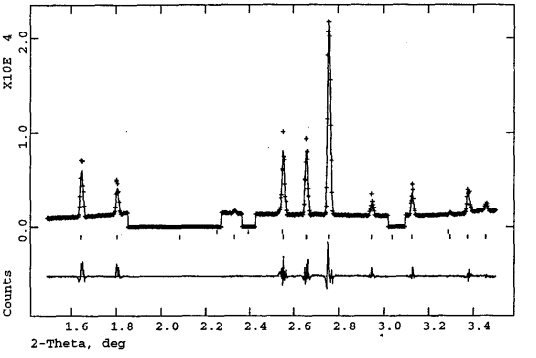

Fig.3 Rietveld profile refinement fit for the 1000 bar H_2O sample