ESRF	**Experiment title:** Pressure dependent filling of the cages in methane clathrate hydrate	**Experiment number**: CH-601
Beamline: ID15A	**Date of experiment**: from: 01.06.1999 to: 08.06.1999	**Date of report**: 10.02.2000
Shifts: 15	**Local contact(s)**: Honkimaki, Veijo	*Received at ESRF:*

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Report:

Gas hydrates are formed by the inclusion of gas molecules into cavities of crystalline host made up of H-bonded water molecules. Methane clathrate is the most abundant and probably the most interesting member of the clathrate family. Large deposits in permafrost regions and beneath ocean floors, offer a potential energy resource. Therefore the p-T dependent quantity of gas stored within the structure is important. Currently the solid-solution model constructed by van der Waals and Platteeuw [1] is used for the calculation of the stoichiometry. A direct consequence of this model is that the cage filling should increase with gas pressure according to a Langmuir isotherm. To establish whether the solid-solution model is suitable in describing the behaviour of methane clathrates, accurate absolute experimental values of the filling of the individual cages are needed which we hoped to obtained from hard X-ray diffraction.

Methane clathrates were formed at variable pressure in Al pressure-cells and analysed *in situ* on the beamline. Samples were prepared at a temperature of 273 K using H_2O at pressures of 25, 35, 60, 140, 500 and 1000 bar as well as one sample at a temperature of 271 K using D_2O prepared at 35 bar. The set-up for the powder diffraction experiment for Rietveld structure refinements is shown in Fig. 1. The instrumental set-up aimed at a good resolution (FWHM; $\Delta d/d \approx 10^{-3}$) and good powder statistics of the sample volumen (630 mm^3, 950 mm^3) with a grain size of 15-20 microns as estimated from our Cryo-SEM investigation; the powder statistics was further improved by continuous rocking of the sample.

The obtained powder pattern was suitable for Rietveld refinement after data correction (geometrical, dead-time, monitor count rate). The refinements were performed using GSAS (Fig. 2). They clearly indicate that the determined filling reach an accuracy of ≈ 2%. In addition data were collected for all samples using an image-plate (positioned instead of the analysator crystal, see Fig. 1); they were treated with the analysis program FIT2D. Unfortunately, the resulting powder diffraction pattern showed insufficient resolution and a clearly worse signal-to noise ratio as compared to the single detector data.

At the present state it is found that the filling of the large cages for methane clathrate nearly follows the generally accepted Langmuir isotherm while it seems that the filling of the small cages deviates from this model (Fig.3). It should also be noticed that the resulting lattice constants were in poor agreement with our values obtained from neutron diffraction on D2B at ILL (Fig. 4) possibly due to some slight change in effective wavelength in the synchrotron run.

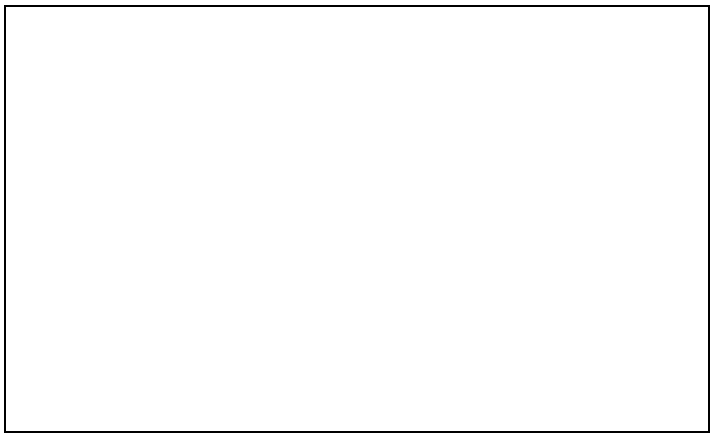

Fig.1 Instrumental set-up for X-ray diffraction (ID15A, ESRF)

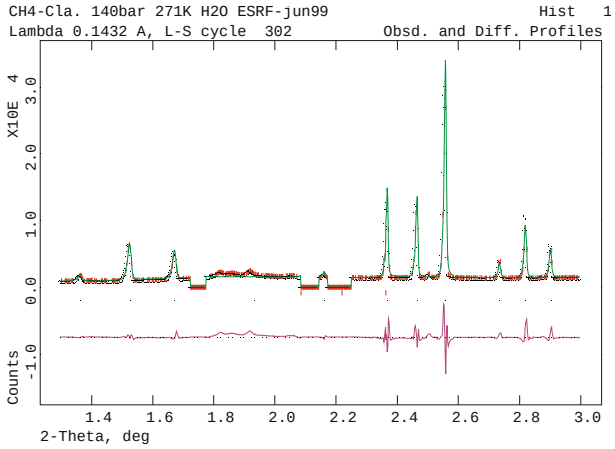

Fig. 2 Rietveld profil refinement fit. Parasitic peaks due to ice Ih were excluded.

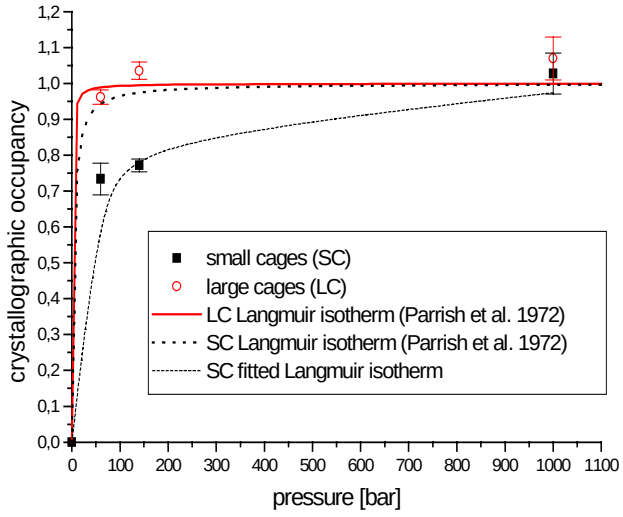

Fig.3 Observed cage filling of CH_4 clathrates

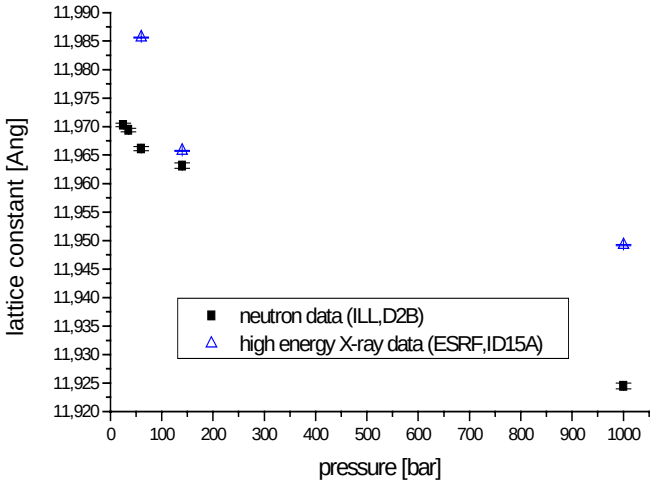

Fig. 4 Observed lattice constants of CH_4 clathrates

Rreference:

1. van der Waals, J. H., and Platteeuw, J. C., *Adv. Chem. Phys.* 2, 1 (1959)