Experimental report

09/02/2016

Proposal:	**7-02-161**	**Council:**	4/2015
Title:	Anomalous dynamics during sI to sII phase transformation in methane hydrate		
Research area:	Physics		

This proposal is a new proposal

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Samples: CH4:5.7D2O

Instrument	Requested days	Allocated days	From	To
IN5	6	4	26/11/2015	30/11/2015

Abstract:

Methane hydrate (MH) is a non-stoichiometric inclusion compound encaging CH4 molecules in a framework of H-bonded water molecules. It has attracted considerable attention over the past decade both for its geophysical relevancy and for its possible energy and environmental applications. Pressure is a key parameter in the study of this system as it induces substantial variations in the size of the cages as well as complete structural rearrangements. However, up to date, only structural and vibrational studies have been carried on high pressure MH, while no information is available on the guest molecule self-dynamics in the different HP polymorphs. In a recent QENS experiment using the HP Paris-Edinburgh apparatus, we unexpectedly observed a clear diffusive dynamics of methane molecules during the sI-sII phase transition. This anomalous dynamics could be linked to the existence of a high-mobility disordered layer between sI and sII coexistence regions [1,2]. Here we propose to shed light on the origin of this motion by measuring the QENS signal of a much larger volume sample (0.5 cm3 of methane hydrate CH4:D2O) contained in a standard HP piston cylinder device, in the 1-5 kbar range.

The experiment was aimed at investigating by quasielastic neutron scattering (QENS) the anomalous diffusive dynamics observed (LTP-6-6_143) during the sI-sII phase transition in methane hydrate formed using the Paris-Edinburgh (PE) high-pressure apparatus, on a much larger sample volume (0.5 cm^3) contained in a liquid compression cell. Unfortunately, we could not form the metastable sII phase this time. The loading of the clathrate in the high pressure vessel was done under liquid nitrogen to avoid temperature-induced destabilisation of the sample. The latter was then compressed at 150 K using a deuterated ethanol-methanol mixture (to avoid sample contamination by the compressing gas) and then warmed up to ambient temperature with the aim to produce the sII phase. The overall procedure was successful but the tightening of the pressure cell compression line at low temperature was a critical step for subsequent compression beyond 5 kbar and warming up under high pressure. The different thermal relaxation of materials systematically caused leaks on the compression line when warming above 170 K. We could detect hints of sII phase formation at the maximum pressure (6 kbar) reachable by the cell, but the pressure was unfortunately soon released during the warming up.

However, thanks to the excellent performances of the instrument IN5, we could measure a clear quasielastic signal in the pure phase sI of methane hydrate, barely visible by our previous measurements. We collected good quality data (see Figure1) within approx. 4 hours per thermodynamic point in the instrumental configuration with incident wavelength of 5 Ang.$^{-1}$. In the assigned 4 days, we measured 18 thermodynamic points along three different isotherms (ambient pressure, 3 and 5 kbar) in the temperature range 100 to 270 K as well as the empty cell and vanadium. This provide, to our knowledge, the first determination of the guest molecule self-dynamics in methane hydrate performed by QENS. Data analysis is currently ongoing to determine the nature of the motion observed (translation and/or rotation). We are confident that these new data will help improving our understanding of the guest-cage interaction in ice clathrates.

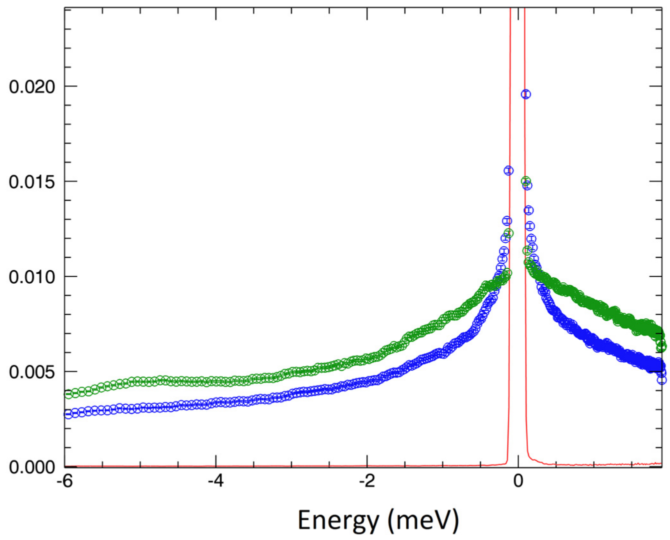

Figure1: *Normalized quasielastic spectra of methane hydrate as measured during the 7-02-161 beamtime at ambient pressure (green) and 5 kbar (blue) at the same temperature of 140 K and momentum transfer of 1.6 Ang.$^{-1}$, as an example. The instrumental resolution is shown in red.*