



	Experiment title: Low frequency collective excitations and sound velocity in low and high pressure phases of methane hydrate	Experiment number: HS-2057
Beamline: ID 28	Date of experiment: from: 02 April 2003 to: 12 April 2003	Date of report: 18.8.2004
Shifts: 21	Local contact(s): Herwig Requardt	<i>Received at ESRF:</i>
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Report:

Three different crystallographic structures of methane hydrate are known today: a low pressure phase I (MH-I) and two high-pressure phases MH-II and MH-III. Methane hydrate structure I forms at moderate pressures (50-100 bar), whereas MH-II and MH-III form at about 10 kbar and 20 kbar, respectively. At the structural phase transition from MH-II to MH-III, the cage structure of the hydrate collapses into a “filled ice” structure, where the guest molecules are found to occupy the channels of the ice network. The transformation from a cage clathrate to a filled ice structure will undoubtedly lead to distinct changes in the dynamical properties of the hydrate and in the hydrophobic interaction between the guest and the host molecules.

We have, for the first time, successfully studied of the phonon dispersion curves of the high--pressure methane hydrate structures. High energy resolution inelastic x-ray scattering (IXS) and diamond anvil cell (DAC) techniques were used to determine the orientationally averaged compressional sound velocities. Combining these findings with the results from diffraction experiments, the elastic properties of the high-pressure phases of methane hydrate were derived. The experiments were performed at the IXS beam line ID28. The x-ray scattering experiments were performed at room temperature ($T=298$ K) and at pressures of 17 kbar and 21 kbar for the MH-II and MH-III sample, respectively.

From diffraction studies MH-II is thought to have a cage-like structure with 1:3.5 methane to water ratio. The stoichiometry of MH-III is known to be $\text{CH}_4 \cdot 2\text{H}_2\text{O}$. At room temperature and pressures of 17 kbar (MH-II) and $p=21$ kbar (MH-III), this leads to samples, which are composed of both methane hydrate and ice VI. A selection of inelastic x-ray spectra of the MH-II and MH-III samples at different wave vector transfers between 2.0 nm^{-1} and 8.9 nm^{-1} is shown in fig. 1a) and 1b), respectively. In order to extract the energy positions $E(Q)$ of the inelastic excitations, the spectra were fitted using a pair of Lorentzian functions for each excitation, convoluted with the experimentally determined instrument resolution (solid line).

The two high intensity peaks display strong dispersions and cannot be quickly move out of the experimental energy window. From the Q-dependence of their energy positions of sound velocities of ~ 12000 m/s and ~ 17000 m/s are determined. These peaks are thus assigned to the transverse and longitudinal acoustic phonons of the diamond anvils. The dispersive excitations marked by the arrows are assigned to the longitudinal acoustic phonons of MH-II/ice VI or MH-III/ice VI. The additional excitations at ~ 12 meV cannot be assigned unambiguously. However, taking the relatively high momentum transfer into account, they are thought to be related to transverse phonons in either ice VI or the respective methane hydrate. The

contribution of the ice VI/MH-II and ice VI/MH-III LA phonons to the IXS signal was disentangled by fitting two Lorentz functions and constraining the energy position of the ice VI feature to values determined from previous IXS measurements and Brillouin light scattering (BLS) results on polycrystalline ice VI. With the separation of the methane hydrate and ice contributions it is possible to obtain the phonon dispersion curves for MH-II and ice VI at $p=17$ kbar (fig. 2a)) and MH-III and ice VI at $p=21$ kbar (fig. 2b)). From the dispersion relation the longitudinal or compressional velocities of sound were derived by fitting a sine-law to the curves and determining the slopes in the $Q \rightarrow 0$ limit. As the bulk modulus B and the density ρ are known from diffraction measurements, we can derive the effective elastic Modulus C , the shear velocity v_s , and the shear modulus G from the compressional sound velocities v_p . The obtained elastic constants are shown in fig. 3.

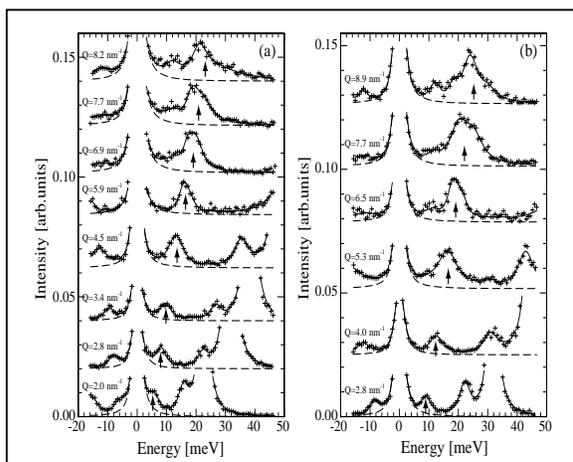


Fig. 1 IXS spectra of the (a) MH-II and (b) MH-III sample are shown for several Q -values. The dispersive excitation marked by the arrows is assigned to the longitudinal acoustic phonons of MH-II or MH-III and ice VI. The LA phonons of methane hydrate and ice VI are visually distinguishable for $Q > 7 \text{ nm}^{-1}$.

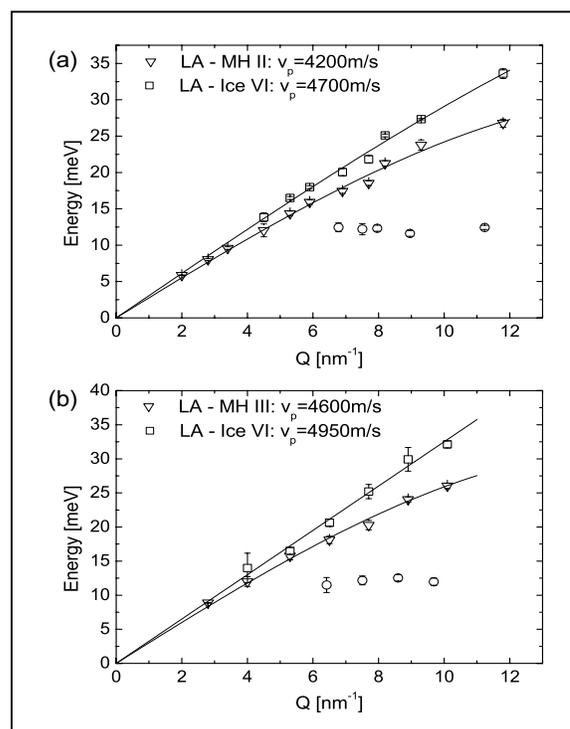
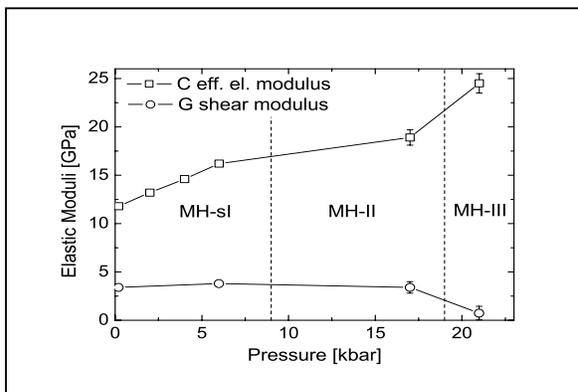


Fig. 2 Dispersion curves of (a) the MH-II and (b) the MH-III sample (open circles). They are shown together with the respective dispersion of ice VI (open triangles).

Fig. 3 The effective elastic modulus C and the shear modulus G , determined from the IXS experiments, are shown together with the pressure dependence of the elastic constants of MH-sI. The lines are guides to the eye only.

In conclusion, we could derive the first experimental values for the elastic properties of the high pressure structures of methane hydrate. The acoustic sound velocities are different from those of ice VI, which can be attributed to the growing influence of the hydrophobic interaction between the guest and host molecules. Furthermore the transition from a cage clathrate to a filled ice structure can be observed in the elastic constants: the effective elastic modulus shows a strong increase attributed to the denser and more compact structure. The decrease in the shear modulus can be related to the layered structure of ice sheets and hydrophobic guest molecules.