ESRF	**Experiment title:** Low frequency collective excitations and sound velocity in natural methane-hydrate	**Experiment number**:
Beamline: ID28	**Date of experiment**: from: 2.2.2002 to: 13.2.2002	**Date of report**: 26.2.2002
Shifts: 30	**Local contact(s)**: Herwig Requardt	*Received at ESRF:*

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Report:

Gas hydrates are a special class of inclusion compounds consisting of water molecules, which form an ice-like network with small guest molecules or atoms included. Even though gas hydrates are formed to 80% out of hydrogen bonded water molecules, some of their properties do not resemble those of ice I_h. One of the intriguing anomalies being the low and glasslike thermal conductivity. The goal of the experiment was to determine the orientationally averaged longitudinal velocity of sound and to observe the guest-host coupling [1] directly in the dispersion relation. It is this guest-host coupling which is thought to give raise to the glasslike thermal conductivity of the clathrate hydrates.

We have successfully performed IXS experiments on synthesised methane and xenon structure I hydrates at the ID28 beamline. Spectra were recorded at around T=100K over a range of 1.2 nm^{-1} to 12 nm^{-1} using the Si(11,11,11) monochromator reflection yielding an energy resolution of 1.5 meV. The xenon hydrate sample was included in our experiment as the measurements on a natural methane hydrate sample recovered from the ocean sea floor by GEOMAR was not feasible due to the high ice contamination of the sample (60%-80%). In order to investigate natural samples the intactness must be assured during recovery, i.e. keeping the sample in stability limits and filtering additional sea-water. Additionally a set of ice I_h spectra was recorded for reference with the same experimental setup.

Figure 1 shows the spectrum of methane hydrate at Q=5 nm^{-1} together with the corresponding ice I_h spectrum. The excitation at ΔE=5 meV displays a strong optic behaviour and furthermore is absent in the ice spectrum. This mode can be attributed to the localised vibrations of the methane molecules inside the cages. The excitation at around ΔE=13 meV is similar to the one in the ice spectrum and can thus be assigned to the longitudinal acoustic (LA) lattice vibration. This LA mode displays about the same energy dispersion as a function of Q as the LA mode in ice. From the dispersion we could derive an orientationally averaged longitudinal velocity of sound of about v=3900m/s for methane hydrate (Fig. 2), which is somewhat higher than in ice I_h.

Of special interest is the region of 1.5 nm^{-1} to 3.0 nm^{-1} where the LA lattice mode intersects the optic guest mode (s. Fig. 2). The absence of the optical guest mode below 2.0 nm^{-1} presumably points towards a mixing of the guest and host modes at the crossing which was predicted form LD calculations [2]. Computer modelling of the intensities of the two modes should enable us to verify in detail the concept of guest-host coupling in the case of methane hydrate.

In the case of xenon hydrate the guest-host coupling is directly visible in the spectra. Figure 3 shows the spectrum for xenon hydrate at 4.5 nm^{-1} and T=100K. In the energy range of 2 meV to 4 meV narrow localised excitations are observable. These correspond to the optic guest modes already seen in inelastic incoherent neutron experiments [3]. The absence of the LA lattice mode visible in the case of methane hydrate points towards a strong interaction and an avoided crossing [1] of the optic guest modes and the acoustic lattice modes. This strong coupling leads to an effective energy transfer between the guest and host lattice vibrations giving raise to a short LA phonon lifetime.

In conclusion we could assign both guest and host lattice modes and identify the guest host coupling for the first time directly in the dispersion relations of xenon and methane hydrate. Thoroughly analysis of the data should yield a direct experimental explanation of the low thermal conductivity of clathrate hydrates.

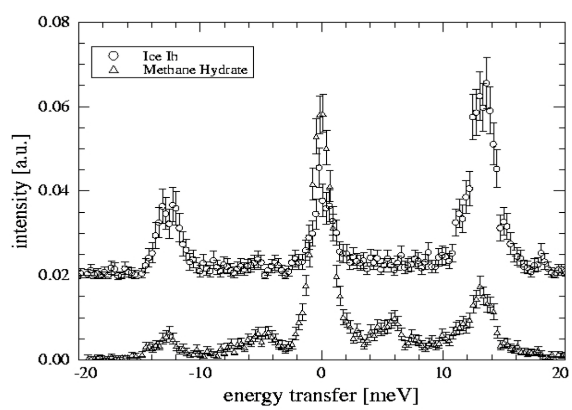

Fig.1 The IXS spectra at Q=5 nm^{-1} and T=100 K of a polycrystalline ice I_h and a methane hydrate sample are shown. The spectra were scaled to the same integral intensity and an offset of 0.02 was introduced. In both spectra an excitation at around 13 meV is observable. This peak was assigned to the longitudinal acoustic lattice mode. In the case of methane hydrate a peak at 5 meV can be additionally seen, it is attributed to the localized guest vibrations inside the cages.

[1] J.S. Tse, V.P. Shpakov, V.R. Belosludov, F. Trouw, Y.P. Handa, W. Press, Europhys.Lett. **54**, 354 (2001)
[2] J.S. Tse, V.P. Shpakov, V.V. Murshov, V.R. Belosludov, J.Chem.Phys. **107**, 9271 (1997)
[3] C. Gutt, J. Baumert, W. Press, J.S. Tse, S. Janssen, J.Chem.Phys. **116**, 3795 (2002)

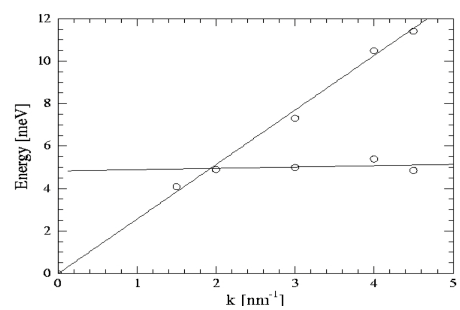

Fig.2 The dispersion curve for methane hydrate is shown. The mode at 5 meV displays a strong optic behavior corresponding to the localized vibrations of the methane molecules inside the water cages. In a first step, the velocity of sound was derived from the linear dispersion of the LA lattice mode.

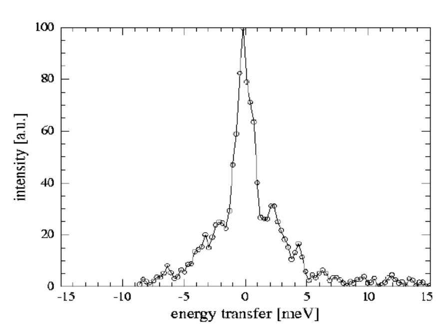

Fig.3 The IXS spectrum of xenon hydrate at Q=4.5 nm^{-1} and T=100 K is shown. The excitations close to the elastic line are attributed to the localized guest vibrations.