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High-pressure Brillouin study on methane hydrate

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Abstract

Acoustic velocities and adiabatic elastic constants of structure I of methane hydrate (MH) have been determined as a function of pressure up to 0.6 GPa at 23 °C by the high-pressure Brillouin spectroscopy developed for a single molecular crystal. The pressure dependence of the acoustic velocities of MH is very similar to that of ice-Ih except for the longitudinal acoustic (LA) velocity. The value of the LA velocity along the $\langle 100 \rangle$ direction of MH at 0.02 GPa is 3.63 km s⁻¹ which is about 7% lower than the average of the LA velocities in the ice-Ih phase at -35.5 °C and atmospheric pressure.

1. Introduction

The great amount of natural methane hydrate (MH) existing in marine deposits is expected to be a major energy resource, while methane in MH is a more effective greenhouse gas than carbon dioxide. Therefore, it is very important to study the elastic and thermal properties of MH in order to make effective use of MH as an energy resource (e.g. the mining of MH from deep-sea sediments). MH consists of a framework of hydrogen-bonded water molecules that form S-cages (12-hedra) and M-cages (14-hedra) including guest methane molecules. This kind of hydrate is classified as structure I (sI). The recent x-ray diffraction, Raman scattering, and decomposition curve measurements [1–3] indicate that structure I methane hydrate (sIMH) exists from about 0.02 GPa to 0.8–1.0 GPa. As for elasticity, although Kieft *et al* [4] have determined the only longitudinal acoustic (LA) velocity for polycrystalline sIMH at -10 °C and 50 bar, no detailed elastic properties have been investigated yet, in spite of their importance. The purpose of this paper is to determine the elastic properties of single-crystal MH, and to investigate the temperature and pressure conditions of dynamical stability in sIMH.

2. Experimental details

Pure water (H₂O) and methane (CH₄) were loaded into a small thin sample chamber (0.4 mm in diameter, 0.04 mm in depth) of a diamond anvil cell (DAC). In order to determine the elastic properties by high-pressure Brillouin spectroscopy, we grew a single crystal of MH in the coexistence state of three phases (liquid H₂O + liquid CH₄ + MH) at about 0.02 GPa and

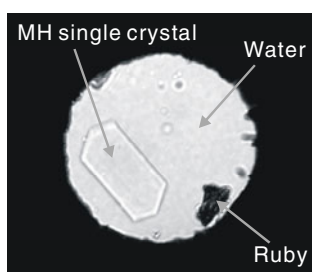


Figure 1. A photograph of a single crystal of MH in a DAC at about 0.02 GPa and 23 °C.

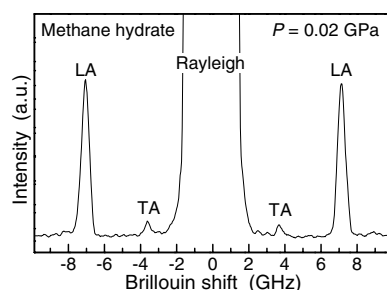


Figure 2. A typical Brillouin spectrum of MH in a 60° scattering geometry at 0.02 GPa and 23 °C. LA and TA indicate the longitudinal and transverse acoustic modes, respectively.

23 °C. This single crystal was identified as sI by comparing our Raman spectra [3] with the earlier ones [5], and was stable below 0.8 GPa [3]. Brillouin spectra were measured in a 60° scattering geometry by using a tandem Fabry–Perot interferometer (JRS). The 514.5 nm line of an argon-ion laser with single-frequency operation was used for excitation with an input power of below 40 mW. A thin sample chamber, where a MH crystal is fully in contact with both the upper and lower diamond anvil faces as shown in figure 1, keeps the wavevector of the observed acoustic phonon parallel to the anvil faces, and enables us to avoid the Brillouin signals from the liquid water surrounding the single-crystal MH.

3. Results and discussion

A typical Brillouin spectrum of sIMH at 0.02 GPa is shown in figure 2. The LA and transverse acoustic (TA) modes were observed. Only one TA signal was observed for sIMH, whereas two TA modes usually appear in the case of solid crystals. This is probably due to the weak intensity in the TA mode and/or high elastic isotropy of sIMH.

By rotating the DAC about the load axis perpendicular to the inner anvil faces, we measured Brillouin frequency shifts (i.e. acoustic velocities) as a function of rotation angle ϕ . Figure 3 shows the dependence on angle ϕ of the Brillouin frequency shifts at about 0.02 GPa. As Brillouin frequency shifts in the 60° scattering geometry ($\Delta\nu_{60}$) are immediately transformed to acoustic velocities (v_{60}) using the equation $v_{60} = \lambda_0 \Delta\nu_{60}$ (λ_0 is the wavelength of the incident light), the scale of acoustic velocity is represented on the right-hand axis in figure 3. The acoustic velocities of LA and TA modes show slight but obvious dependence on angle ϕ . This result implies that sIMH is almost elastically isotropic. By applying the least-squares fitting method to the experimental dependence on angle ϕ of the acoustic velocities and the solution for acoustic velocities from the Christoffel equation [6], we obtained the best-fitted theoretical curves—indicated by solid curves in figure 3—which yielded three optimized ratios of elastic constants to density: $C_{11}/\rho = 13.2 \times 10^6 \text{ m}^2 \text{ s}^{-2}$, $C_{12}/\rho = 7.07 \times 10^6 \text{ m}^2 \text{ s}^{-2}$, and $C_{44}/\rho = 3.76 \times 10^6 \text{ m}^2 \text{ s}^{-2}$ at 0.02 GPa and 23 °C. From these values, the elastic anisotropy $A (=2C_{44}/(C_{11} - C_{12}))$ is estimated to be 1.23. If a crystal is elastically isotropic, two TA modes are degenerate and the elastic anisotropy A becomes 1. Therefore, the elasticity of sIMH is very close to isotropic unlike those of some typical pressure-induced molecular crystals with cubic structure (such as CO₂, ice-VII, H₂S, Kr, CH₄ [7]) showing $A = 2\text{--}6$ under high pressures; this is probably characteristic of sIMH.

Provided that A is 1 for sIMH, the LA and TA velocities correspond to $(C_{11}/\rho)^{1/2}$ and $(C_{44}/\rho)^{1/2} = [(C_{11} - C_{12})/(2\rho)]^{1/2}$, respectively. Therefore, we calculated that

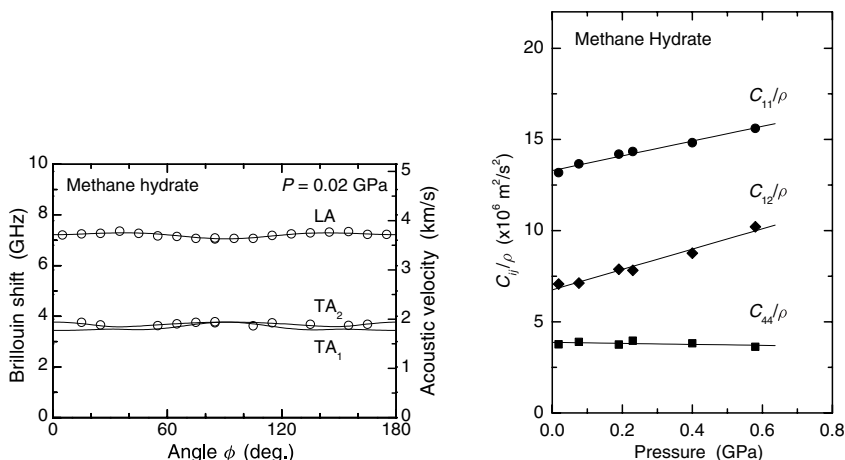


Figure 3. Brillouin frequency shifts (acoustic velocities) as a function of rotation angle ϕ at 0.02 GPa and 23 °C. Open circles indicate the experimental values and solid lines indicate the theoretical best-fitted curves. LA, TA₁, and TA₂ represent the longitudinal, slow transverse, and fast transverse acoustic modes, respectively.

Figure 4. The pressure dependence of C_{ij}/ρ for sIMH at 23 °C.

$C_{11}/\rho = 13.7 \times 10^6 \text{ m}^2 \text{ s}^{-2}$, $C_{12}/\rho = 6.49 \times 10^6 \text{ m}^2 \text{ s}^{-2}$, and $C_{44}/\rho = 3.62 \times 10^6 \text{ m}^2 \text{ s}^{-2}$, by substituting the average velocities $v_{LA} = 3.71 \text{ km s}^{-1}$ and $v_{TA} = 1.90 \text{ km s}^{-1}$ estimated from figure 3 into the above relations. The differences between the C_{ij}/ρ from the least-squares method and those from the assumption $A = 1$ are within 8%. For the present, we employed the results from the least-squares fitting method, because the acoustic velocities in figure 3 show a slight dependence on angle ϕ .

Using the above procedure, carried out at various pressures, the pressure dependence of C_{ij}/ρ for MH was obtained up to 0.6 GPa, as shown in figure 4. It is clear that C_{44}/ρ is almost constant or slightly decreasing with pressure in contrast to the positive pressure dependences of C_{11}/ρ and C_{12}/ρ , which means that sIMH becomes weaker against shear stress in comparison with uniaxial compression.

Once the C_{ij}/ρ have been determined, we can easily calculate the acoustic velocities propagating in any direction. Thus the pressure dependences of the acoustic velocities propagating along the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions are obtained as shown in figure 5, compared with the average acoustic velocities of ice-Ih at -35.5 °C [8]. One can see the similarity between the pressure dependences of the acoustic velocities for MH and ice-Ih, except as regards the LA velocity. The value of the LA velocity of sIMH is about 7% lower than the average LA velocity of ice-Ih, which means that MH crystal is softer than ice-Ih. From the pressure dependence of the acoustic velocities, the LA velocity propagating along the $\langle 100 \rangle$ direction can be calculated as 3.65 km s^{-1} at 50 bar and 23 °C. This value is at least 10% larger than the average LA velocity determined by Kieft *et al* (3.3 km s^{-1}).

Finally, we will calculate the pressure dependences of three adiabatic elastic constants of sIMH. Recently, Hirai *et al* [9] have determined a lattice constant of sIMH as a function of pressure on the basis of *in situ* x-ray diffractometry at room temperature. In order to determine the density of sIMH from a lattice constant, we require the occupancy rate of the guest methane molecules in the host S- and M-cages. Hence we calculated the pressure dependence of the density from the lattice constant of sIMH, assuming that the cage occupancies are 100 and 75%. Then, these results and the present values of C_{ij}/ρ yielded the adiabatic elastic constants C_{ij}

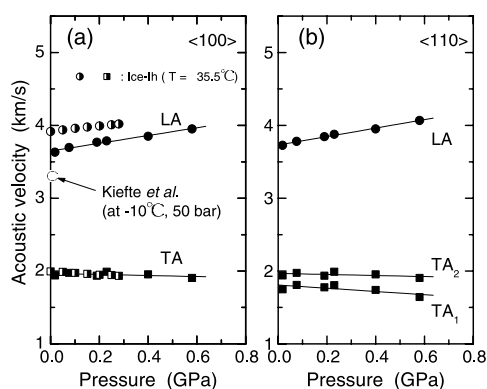


Figure 5. Pressure dependences of the acoustic velocities of MH propagating along (a) $\langle 100 \rangle$ and (b) $\langle 110 \rangle$ directions at 23 °C, with the average velocities of ice-Ih at -35.5 °C.

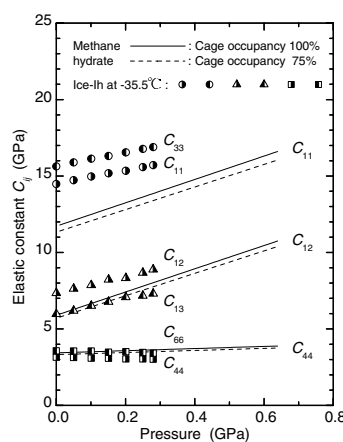


Figure 6. Pressure dependences of the elastic constants of sIMH (at 23 °C) and ice-Ih (at -35.5 °C).

as a function of pressure. The results are shown in figure 6 compared with the elastic constants of ice-Ih at -35.5 °C. Solid lines and broken lines indicate the adiabatic elastic constants for the cage occupancies 100 and 75%, respectively. Unfortunately, for the present, it is difficult to obtain accurate cage occupancies in the sIMH crystal grown in the DAC. The true adiabatic elastic constants of sIMH may lie between the solid and broken lines for each C_{ij} . Figure 6 also shows the similar pressure dependences of sIMH and ice-Ih—except as regards C_{11} and C_{33} . C_{11} for sIMH is about 20% (25%) smaller than C_{11} (C_{33}) for ice-Ih at around atmospheric pressure. It is clear that sIMH is softer than ice-Ih.

4. Conclusions

The acoustic velocities and the adiabatic elastic constants of sIMH have been determined for the first time at pressures up to 0.6 GPa at 23 °C by high-pressure Brillouin spectroscopy. From the present results, it turns out that the cage structures in gas hydrates may induce elastic isotropy, and the sIMH becomes weaker and more fragile against shear stress with increasing pressure, which provides useful information for surveys for the size estimation of and the safe mining of MH from deep-sea deposits.

Acknowledgment

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