Elastic Properties of Water and Ice VI Studied by Brillouin Scattering

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The pressure dependence of acoustic velocities and refractive index of liquid H₂O and D₂O have been determined up to 1.05 GPa at room temperature. For the tetragonal ice VI from $P = 1.05$ to 2.10 GPa, we present the detailed method of the determination of six elastic constants, which are compared with the recent result at 0.72 GPa and 271 K by Tulk *et al.* [Brillouin scattering, elastic property, water, ice VI, elastic constant]

1. Introduction

Water and ice are important materials in nature. Water can exist in many crystalline forms under different conditions of pressure and temperature. An interesting variety of these polymorphisms is mainly due to the hydrogen bond and the structural versatility of H₂O molecules. At room temperature, compression of water leads to a tetragonal ice VI at pressures above 1.05 GPa and further to a cubic ice VII above 2.10 GPa.

High-pressure Brillouin spectroscopy is a useful method to study elastic properties of molecular single crystals grown in a diamond anvil cell (DAC): Acoustic velocities for any direction, the refractive index, and adiabatic elastic constants can be exactly determined by only Brillouin scattering measurements with *in situ* identification of the crystal orientation at each pressure [1].

Polian and Grimsditch [2] made the Brillouin study only at a scattering geometry of 180° and observed the pressure dependence of nv in ice VI and VII phases without identification of the crystal orientation. Very recently, we have obtained the mapping of sound velocities for all directions in ice VI and VII (up to 8 GPa), and determined the pressure dependence of respective six and three elastic constants [3,4].

In this paper, we present the pressure dependence of the acoustic velocity (v) and the refractive index (n) of liquid H₂O and D₂O, and show the pressure dependence of 6 elastic constants of tetragonal H₂O ice VI in the pressure range from 1.05 to 2.10 GPa at 300 K. These typical values of elastic constants are compared

with those determined for ice VI at 0.72 GPa and 271 K by Tulk *et al.* [5], by concerning with the fitting method for the determination of 6 elastic constants.

2. Experiment

A Sandercock tandem Fabry-Perot interferometer was used in the triple-pass arrangement for Brillouin scattering measurements (see Fig. 1). The Brillouin frequency shifts ($\Delta\nu$) at 90° and 180° scattering geometries with the DAC are related to the v as follows;

$$\Delta\nu_{90} = \sqrt{2} v_{90} / \lambda_0 \quad (1), \quad \Delta\nu_{180} = (2n) v_{180} / \lambda_0 \quad (2),$$

where λ_0 is a wavelength of the incident laser line, and $\Delta\nu_{90}$ is independent of the n . For the isotropic medium, v_{90} is equal to v_{180} . Therefore, by using Eqs. (1) and (2), we can get

$$\Delta\nu_{180} / \Delta\nu_{90} = \sqrt{2} n. \quad (3)$$

As a result, the refractive index n can be determined by measuring $\Delta\nu_{180}$ and $\Delta\nu_{90}$.

A single crystal of ice VI was grown by increasing the pressure on a seed crystal, which coexists with the water at about 1.05 GPa at 300 K. The seed crystal in the DAC presents sometimes a typical dipyrmaid shape as shown in Fig. 2. The (101) plane of the tetragonal H₂O ice can be clearly seen and recognized, as indicated

Fig. 1. Experimental set up for 90° Brillouin scattering under high pressure with DAC. PR1, PR2 and PR3 are used for 180° scattering measurements.

Fig. 2. Photograph of single crystal of ice VI coexisting with water at 1.05 GPa and 300 K. Crystal facets characterized by the tetragonal ice VI are clearly observed.

previously by x-ray studies [6]. In order to study the elastic properties of ice VI, we used the single crystal grown from this type of seed [showing its (101) plane parallel to the culet faces of diamonds], because we need, as described later, the initial guess for the orientation of a single crystal in the DAC.

3. Theoretical Basics

From the secular equation for the propagation of elastic wave in a tetragonal system, Every [7] derived the relation between acoustic velocities for arbitrary direction and six elastic constants (C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , C_{66}). The acoustic velocities are expressed as a function of nine parameters as follows:

$$v_j = g_j(C_{11}/\rho, C_{12}/\rho, C_{13}/\rho, C_{33}/\rho, C_{44}/\rho, C_{66}/\rho, \theta, \phi, \chi), \quad (4)$$

where ρ is density, the subscript j ($= 0, 1, 2$) of the velocity v_j indicates LA, TA₁ (slow), and TA₂ (fast) modes, respectively, and Euler angle (θ, ϕ, χ) relates the laboratory frame (X, Y, Z) to the crystal reference frame (x, y, z). In order to determine three Euler angles (= crystal orientation) and six elastic constants at each pressure, we applied a computerized least-squares fit between calculations $g_j(\phi_i)$ and experimental velocities (ϕ_i, v_{ji}) as a function of angle ϕ_i ,

$$J = \sum_{ij} [g_j(\phi_i) - v_{ji}]^2, \quad j = 0, 1, 2 \quad (5)$$

where, after the set of initial values for nine parameters, J is minimized by systematically varying the nine parameters until the fit is optimized. Then, according to the initial values set for nine parameters, we find two stability cases in which J is minimized

Fig. 3. Two cases (A) and (B) which are elastically equivalent each other for tetragonal lattice, and the corresponding matrix of elastic constants.

Fig. 4. (a) Pressure dependence of Brillouin frequency shifts at 90° and 180° scatterings for liquid H₂O (open circles) and D₂O (solid circles). Values of 90° scattering indicate acoustic velocity simultaneously. (b) Pressure dependence of refractive indices (n) for liquid H₂O (open circles) and D₂O (solid circles) at 300 K.

with the optimum fit. Therefore, we should identify one true point, which is different from the cubic system [1, 3].

Let us investigate the origin of two stability points which appear on the least-squares fit for the tetragonal system. As shown in Fig. 3(A), the tetragonal lattice is usually defined in a coordinate of (x, y, z) - case A -. Then, the (a, a, c) lattice indicates the matrix of adiabatic elastic constants as seen Fig. 3(A). However, another choice can be possible as shown in Fig. 3(B); 45° rotated (x', y', z) system about z -axis - case B -. This (a', a', c) lattice is not crystallographically identical to the (a, a, c) lattice, but these two lattices can not be elastically distinguished. The matrix of elastic constants for (a', a', c) lattice is easily derived as shown in Fig. 3(B). This is the reason why we find two (A and B) cases in which two stability points appear with the optimum fit. As a result, we need another information about the orientation of the tetragonal lattice in the DAC, in order to determine 6 elastic constants. As described in a later part, we used (101) or ($\bar{1}01$) plane of a dipyramid seed-crystal as the initial guess of the orientation of growing tetragonal H₂O-VI lattice.

4. Results and Discussion

For the liquid H₂O and D₂O at pressures up to about 1.2 GPa and 300 K, we determined the pressure dependence of v and n . A high-pressure Brillouin spectrum of water at 90° scattering geometry shows two signals: A strong peak indicates the Δv_{90} , which gives us the acoustic velocity by Eq.(1) as shown in Fig.4(a). The weak peak can be detected simultaneously as the 180° scattering signal (Δv_{180}), which is due to a laser beam reflected from the output diamond that serves as incident light. Figure 4(a) shows the pressure dependence of Δv_{90} (sound velocity) and Δv_{180}

of liquid H_2O and D_2O below 1.2 GPa. Because the liquid is acoustically isotropic, the velocity is the same for any direction. Therefore, we determined the pressure dependence of n by using Eq. (3). The n of liquid H_2O and D_2O , as seen in Fig. 4(b), show almost the same values and increase with pressure up to $n = 1.41$ near the freezing point. The sound velocity and the refractive index show reasonable pressure dependence, and their values for liquid H_2O and D_2O are almost no difference.

For tetragonal H_2O and D_2O ice VI, we present the method of determinations for the velocity mapping and 6 elastic constants as

Fig. 5. The rotational dependence of Brillouin frequency shift at 180° scattering geometry (solid D_2O at $P = 2.0$ GPa).

a function of pressure. Since the ice-VI crystal is usually birefringent, to estimate the anisotropic degree of refractive index, we measured the angular dependence of Δv_{180} at 180° scattering geometry [see Eq. (3)]. Since the velocity v_{180} is independent of the rotation (ϕ) along the load axis of the DAC, we can estimate the direction dependence of n by rotating the incident-light polarization (i.e., rotation of the DAC in 10° intervals as shown in Fig. 5). The ϕ dependence of Δv_{180} for the LA mode was measured at $P = 2.0$ GPa as shown in Fig. 5. The Δv_{180} is almost independent of ϕ , that is, $\Delta v_{180} = 26.85 \pm 0.135$ GHz. This result indicates that the birefringence is less than about 1%, which agrees with the previous study [2] by measuring Brillouin shifts with two cases of the incident light polarized parallel and perpendicular to the crystal axes at 180° scattering geometry. Therefore, from our analysis of sound velocity, we can neglect the anisotropy of the refractive index in the ice VI within the experimental error on the measurements of Brillouin frequency shifts.

Brillouin measurements were made at 90° scattering geometry in 10° intervals of the rotation angle ϕ about the load axis of the DAC. The observed Brillouin shifts, that is, sound velocities for H_2O ice at 1.23 GPa [from Eq. (1)], are plotted as a function of ϕ by open symbols in Fig. 6. To analyze the angular dependence of velocities of the LA and the two TA_1 (slow) and TA_2 (fast) modes at each applied pressure, we used Eq. (4). The computerized least-squares fit was applied to determine the elastic constants and Euler angles (orientation of a H_2O single crystal grown in the DAC). The best-fit calculations are represented by the solid lines in Fig. 6 for different initial sets of parameter values. Therefore, we met two cases in which J (Eq. 5) was minimized with the optimum fit. In Fig. 6 we can see the final values of fitted 8 parameters and the error of least-squares fit (lse) for two cases. How do we select the true one from two cases? As mentioned above, we grew up the ice

Fig. 6. Brillouin frequency shifts and acoustic velocities of LA, TA_2 , and TA_1 modes as a function of angle ϕ at a 90° scattering geometry for H_2O ice VI at $P = 1.23$ GPa. Open symbols indicate experimental points, and the solid lines represent the fitted velocities. For cases (A) and (B), fitted parameters are indicated with the error of fitting (lse). The parentheses for case (B) shows the calculated values from case (A) by the use of relation in Fig. 3.

Fig. 7. Velocity mapping in typical planes for H₂O ice VI at $P = 1.23$ GPa and 300 K.

VI single-crystal showing its (101) or ($\bar{1}01$) plane parallel to the culet faces of diamonds. Therefore, this situation indicates that the Euler angle χ should be nearly 0° or 90° . As seen in Fig. 6, case (A) shows $\chi = 1.4^\circ$, and case (B) does $\chi = 46.4^\circ$. As a result, case (A) yielded the perfect solution of $C_{11}/\rho = 24.1 \text{ km}^2\text{s}^{-2}$, $C_{12}/\rho = 8.8 \text{ km}^2\text{s}^{-2}$, $C_{13}/\rho = 10.8 \text{ km}^2\text{s}^{-2}$, $C_{33}/\rho = 20.3 \text{ km}^2\text{s}^{-2}$, $C_{44}/\rho = 4.6 \text{ km}^2\text{s}^{-2}$, $C_{66}/\rho = 4.3 \text{ km}^2\text{s}^{-2}$ and the crystal orientation $\theta = 43.7^\circ$ and $\chi = 1.4^\circ$ within an accuracy of $\pm 2\%$. Here, it is noted that the $\chi = 46.4^\circ (= 45^\circ + 1.4^\circ)$ for case (B) indicates the 45° rotation of case (A) around z -axis. From the relation of $C'_{11} = (C_{11} + C_{12})/2 + C_{66}$, $C'_{12} = (C_{11} + C_{12})/2 - C_{66}$, $C'_{13} = C_{13}$, $C'_{33} = C_{33}$, $C'_{44} = C_{44}$, and $C'_{66} = (C_{11} - C_{12})/2$ stated in Fig. 3, the parameter values are calculated, and are shown in parentheses at case (B) in Fig. 6. The agreement between this calculated value and the fitted one is very good.

Once the nine parameters were determined, the acoustic velocities [$v = (C_{ij}/\rho)^{1/2}$] could be calculated for all directions. The typical velocity mapping of ice VI at $P = 1.23$ GPa is shown in Fig. 7. Next, we show the pressure dependence of acoustic velocities in typical $\langle 100 \rangle$ and $\langle 110 \rangle$ directions of H₂O and D₂O ice VI in Fig. 8. The acoustic velocity in a liquid shows discontinuous changes to

Fig. 8. The pressure dependence of acoustic velocities for (a) $\langle 100 \rangle$ and (b) $\langle 110 \rangle$ directions at 300 K in tetragonal H₂O (solid line) and D₂O (broken line) ice up to 2.10 GPa. The acoustic velocity in liquid H₂O and D₂O show discontinuous changes to three acoustic modes at the freezing pressure of $P = 1.05$ GPa.

Fig. 9. Pressure dependence of refractive index at 300 K in a liquid water up to 1.05 GPa and tetragonal ice VI up to 2.1 GPa. Open squares indicate H₂O and solid circles do D₂O.

Fig. 10. Pressure dependence of elastic moduli in a liquid H₂O ($C = \rho v^2$) up to 1.05 GPa and tetragonal H₂O ice VI (C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66}) up to 2.10 GPa at 300 K.

LA, TA₂ and TA₁ in ice VI, and they increase with pressure. The distinction in acoustic velocity for H₂O ice (v_{H_2O}) and D₂O ice (v_{D_2O}) is understood by the kinetic theory, $v_{H_2O}/v_{D_2O} = (M_{D_2O}/M_{H_2O})^{1/2} = 1.054$, where M_{D_2O} and M_{H_2O} are the molecular weight of D₂O and H₂O, respectively. This relation is approximately obeyed at each pressure.

Furthermore, we can calculate the acoustic velocity (v_{180}) along the direction perpendicular to diamond interfaces, which is available to determine the refractive index (n) by using Eq. (3). From the Δv_{180} measured at 180° scattering geometry, we can obtain the pressure dependence of n for H₂O and D₂O ice VI as shown in Fig. 9. The uncertainties in the measured frequency shifts and in the determined refractive index are about $\Delta(\Delta v)/\Delta v = \pm 1\%$ and $\Delta n/n = \pm 2\%$, respectively. At the freezing point, n shows a discontinuous increase of about 4% and, moreover, increases gradually with pressure up to $n = 1.48$ at $P = 2.10$ GPa. The n of H₂O ice shows almost the same values as D₂O ice, and the present results are in good agreement with those estimated by Polian and Grimsditch [2].

In Fig. 10 we show six elastic constants for H₂O ice VI as a function of pressure between 1.05 and 2.10 GPa by using the pressure dependence of ρ from X-ray studies [8]. In Table 1 our

Table 1. Elastic moduli (GPa) in tetragonal H₂O ice VI determined by the present study and Tulk *et al.* [5], and the calculated values by operating a 45° rotation of crystalline axes about z-axis for the system of Tulk *et al.*

	Elastic moduli (GPa)					
	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
Present study ($P = 1.23$ GPa, $T = 300$ K)	32.8	11.8	14.7	27.8	6.3	5.9
Tulk <i>et al.</i> [5] ($P = 0.72$ GPa, $T = 271$ K)	26.8	14.5	12.8	26.2	6.3	10.4
45° rotation around z-axis for Tulk <i>et al.</i>	31.1	10.3	12.8	26.2	6.3	6.1

typical values of $P = 1.23$ GPa are listed with recent results of ice VI at 0.72 GPa and 271 K by Tulk *et al.* [5]. The difference exists in their relative values and in their inequality of 6 elastic constants: present results; $C_{11} > C_{33}$, $C_{12} < C_{13}$, $C_{44} > C_{66}$, Tulk *et al.*; $C_{11} \approx C_{33}$, $C_{12} > C_{13}$, $C_{44} < C_{66}$. If we operate a 45° rotation of crystalline axes around z-axis for the system of Tulk *et al.*, the calculated values which are very close to our present results were obtained as listed in Table 1. Tulk *et al.* used a large high-pressure cell made from a steel block, $7 \times 7 \times 10$ cm, and they obtained the initial guess of two Euler angles, by using the extinction method of polarized light due to birefringence of ice VI [5]. (birefringence is less than about 1%)

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