Cauchy Relation in Dense H$_2$O Ice VII

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By high-pressure Brillouin spectroscopy, sound velocities for all directions and three elastic constants of cubic ice VII have been determined up to 8 GPa at room temperature, with *in situ* identification of the orientation of the ice VII single crystal grown in a diamond-anvil cell. We have found the unusual result that the Cauchy relation ($C_{12} = C_{44}$) holds at every pressure for ice VII. This result suggests that the interactions between the atoms can be described by central forces. By a force-constant analysis of elastic constants, we show that the self-clathrate structure of two diamond-type sublattices can induce effectively central forces, and discuss their broad stability fields in the ice VII phase.

The behavior of H$_2$O ice at high pressure is of fundamental importance in condensed matter and planetary science. An interesting variety of ice polymorphism exists under different conditions of pressure and temperature [1]. At room temperature, compression of liquid water leads to a tetragonal ice VI phase at pressures above 1.05 GPa and further to a cubic ice VII phase above 2.1 GPa. However, above this pressure the phase diagram simplifies down to only two VII and VIII phases. In these higher-pressure phases, high density is achieved by forming "self-clathrate" structures [1–4]. The structure of ice VII can be built up, as shown in Fig. 1, from two interpenetrated but unconnected diamond-type (ice I_c) sublattices of oxygen atoms, where the oxygen atoms form a body-centered cubic (bcc) lattice and the protons are disordered within Pauling's ice rules (ice VIII is the proton-ordered form of ice VII). A further feature of ice VII that is related to the unconnected sublattices is that only four of the eight nearest-neighbor oxygen atoms are hydrogen bonded to the central oxygen atom.

For pressure-induced H$_2$O ice at pressures above 1.05 GPa and 300 K, Polian and Grimsditch [5,6] measured the Brillouin spectra only at a scattering geometry of 180° and observed the pressure dependence of nv in ices VI and VII up to 67 GPa without identification of the crystal orientation, where nv is the product of the refractive index and the sound velocity, respectively [see Eq. (3)]. From the pressure dependence of nv, they observed the VI → VII phase transition at about $P = 2.1$ GPa, and moreover claimed the possible existence of a symmetric ice X phase above 44 GPa. Around this region, however, Pruzan, Chervin, and Canny [7] have found no evidence of ice X in the Raman spectra, and Hemley *et al.* [8] have indicated from a synchrotron x-ray diffraction investigation that the bcc oxygen sublattice of ice VII persists to 128 GPa. Therefore, ice VII has a broad stability field at room temperature.

Elastic properties determined by high-pressure Brillouin scattering [9] shed new light on the characteristic behavior of polymorphic varieties of ice, and provide some insight into the forces of interaction. The sound velocity for the probed acoustic phonon, which can be determined from the measured Brillouin frequency shift, is sensitively dependent on the crystal orientation even for a cubic crystalline system [10]. Since the crystal orientation cannot be controlled when a gaseous or liquid sample is solidified
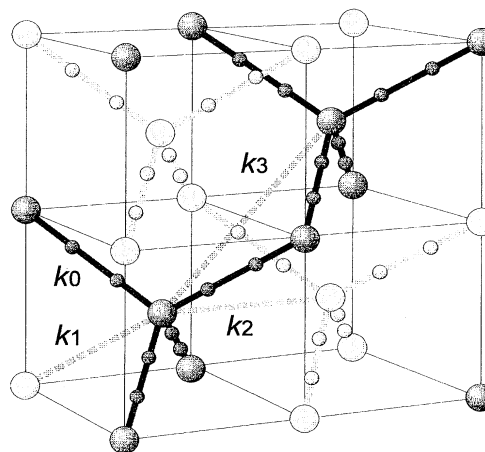

FIG. 1. The average structure of ice VII. Large spheres are oxygen atoms. Small spheres are possible hydrogen atom sites which have 50% average occupancy. The cubic cell is drawn to emphasize the bcc arrangements of oxygen atoms. Two interpenetrating I_c sublattices are distinguished by fully and partially shaded atoms and bondings. Four of the eight nearest-neighbor oxygen atoms are hydrogen bonded to the central oxygen atom. Force constants k_0, k_1, k_2, and k_3 are set for the nearest-neighbor hydrogen-bonded O—H···O (own 4 pairs), the nearest-neighbor nonbonded oxygen atoms (4 pairs), second-neighbor nonbonded oxygen atoms (6 pairs), and third-neighbor weakly bonded oxygen atoms (own 12 pairs), respectively.

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at high pressures in a diamond-anvil cell (DAC) [11], we need to identify accurately the axis orientation of a molecular single crystal.

In this Letter, we present the first measurements of acoustic velocities for all directions and elastic constants (C_{11}, C_{12}, and C_{44}) of a H_2O ice VII single crystal at pressures to 8 GPa, with in situ identification of the crystal orientation. The important result is the finding of the Cauchy relation ($C_{12} = C_{44}$) which suggests that the interactions between the atoms can be described by central forces. By theoretical analysis of the elastic constants, we investigate the forces of interaction by taking into consideration the characteristics of two interpenetrated (but unconnected) diamond-type sublattices, and discuss the broad stability field in the high-pressure densest ice VII phase.

Ice VII in the DAC is usually polycrystalline, because it is produced through the phase transition of solid VI → solid VII at room temperature [5]. In order to grow a single crystal of ice VII, we used a new route through the direct phase transition of liquid H_2O → solid ice VII above the triple point ($P = 2.2$ GPa, $T = 355$ K) of liquid and solid VI and VII phases. For Brillouin scattering measurements, the 514.5-nm argon-ion laser line (λ_0) with a single mode was used. The heart of the apparatus was a plane piezoelectrically scanned Fabry-Pérot interferometer, which was used in a five-pass configuration [10,12]. The Brillouin frequency shifts ($\Delta\nu$) at 60°, 90°, and 180° (angles between the incident and the scattered beams) scattering geometries with the DAC are related to v as follows [9]:

$$\Delta\nu_{60} = v_{60}/\lambda_0, \tag{1}$$

$$\Delta\nu_{90} = \sqrt{2}\,v_{90}/\lambda_0, \tag{2}$$

and

$$\Delta\nu_{180} = (2n)v_{180}/\lambda_0. \tag{3}$$

In order to apply the new method of high-pressure Brillouin spectroscopy [10,12], we measured Brillouin shifts at 90° and 60° scatterings, i.e., acoustic velocities in 10° intervals of the rotation angle ϕ about the load axis of the DAC in the laboratory frame. The observed Brillouin shifts at 60° scattering and at $P = 4.7$ GPa, i.e., acoustic velocities, are plotted as a function of ϕ as open circles in Fig. 2. The square of velocities of a cubic crystal can be expressed as a function of six parameters: $v_i^2 = f(C_{11}/\rho, C_{12}/\rho, C_{44}/\rho, \theta, \phi, \chi)$, where the subscript i indicates longitudinal (LA), slow (TA_1), and fast (TA_2) transverse modes and ρ is the density, and (θ, ϕ, χ) are the Euler angles relating the laboratory frame (DAC) to the crystal reference frame. A computerized least-squares fit was applied to determine elastic constants and Euler angles by systematically varying the six parameters until the fit was optimized. The best-fit calculations are represented by dotted lines in Fig. 2. There is excellent agreement between the measured and the fitted values, which yielded, for example, $C_{11}/\rho = 32.7$, $C_{12}/\rho = 18.2$, and $C_{44}/\rho = 18.9$ GPa cm³ g⁻¹ at 4.7 GPa.
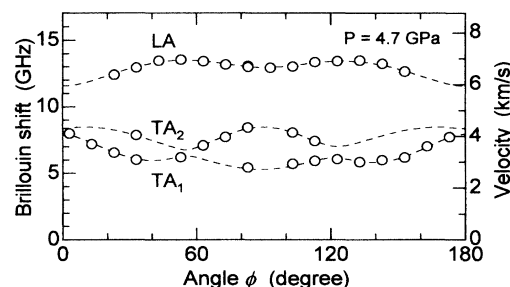

FIG. 2. Brillouin frequency shifts and acoustic velocities of LA, TA_1, and TA_2 modes as a function of angle ϕ at a 60° scattering geometry for solid H_2O at 4.7 GPa. Open circles indicate experimental points, and the dotted lines represent the calculated best-fit velocities.

Once the six parameters were determined, the acoustic velocities could be calculated for all directions. Figure 3 shows the first presentation of ice VII sound velocities for typical directions as a function of pressure between 2.1 and 8 GPa. Furthermore, the pressure dependence of elastic constants C_{11}, C_{12}, and C_{44} was determined by use of the pressure dependence of ρ from x-ray studies [13] (see Fig. 4). We can find at each pressure that C_{12} is nearly equal to C_{44} within the experimental error. This relationship of $C_{12} = C_{44}$ is well known as the Cauchy relation [14,15], which is unusual except for ionic crystals at room temperature [14]. This Cauchy relationship will
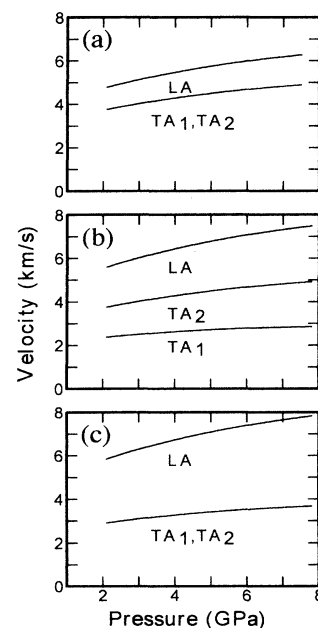

FIG. 3. The pressure dependence of sound velocities, which were calculated by the use of C_{11}/ρ, C_{12}/ρ, C_{44}/ρ, and Euler angles for (a) $\langle 100 \rangle$, (b) $\langle 110 \rangle$, and (c) $\langle 111 \rangle$ directions in cubic H_2O ice VII at 300 K. LA, TA_1, and TA_2 are longitudinal, slow and fast transverse modes, respectively.
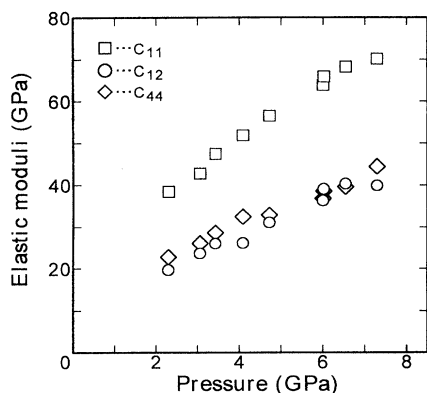
FIG. 4. The pressure dependence of elastic constants C_{11}, C_{12}, and C_{44} of cubic H_2O ice VII at 300 K. At each pressure C_{12} is nearly equal to C_{44} within the experimental error.

be fulfilled with the following two conditions: (1) every lattice particle occupies a center of symmetry, and (2) in a crystal all forces are central, i.e., act along lines joining the centers of the atoms. Condition (1) is just satisfied if the structure of the ice VII is characterized mainly by the bcc arrangement of oxygen atoms, i.e., the disordered protons can contribute slightly to elastic constants. This idea is based on our above experimental result, and can be justified by the application of the force-constants model. Condition (2) means that the atoms interact with central forces, i.e., central forces may play a significant role in the self-clathrate ice VII. The values of the elastic constants at $P = 4.7$ and 6.5 GPa are listed in Table I with those of typical materials. In ionic crystals of NaCl and KCl, the Cauchy relation is well fulfilled at 1 bar and room temperature [14], because the principal interaction is just Coulomb forces and, therefore, central in nature. The C_{11}, C_{11}-C_{12}, and C_{44} of NaCl were measured by Brillouin scattering as a function of pressure up to 4 GPa in 1976 [16]. Whitfield, Brody, and Bassett [16] did not investigate the Cauchy relationship at high pressure, because the estimated errors

TABLE I. Elastic constants (in GPa) of H_2O ice VII under high pressures at 300 K, and typical cubic crystals for comparison.

	Pressure P	C_{11}	C_{12} (GPa)	C_{44}
H_2O VII	4.7 GPa	57	31	32
	6.5 GPa	69	40	39
NaCl[a,b]	1 bar	48.6	12.7	12.8
KCl[a]	1 bar	40	6.2	6.2
Si[a]	1 bar	166	64	79
Ge[a]	1 bar	129	48	67
Ar[c]	4.0 GPa	32	16.3	11.6

[a]Reference [14].
[b]Reference [16].
[c]Reference [15].

in C_{12} and C_{44} are $\pm 6\%$ and $\pm 3\%$, respectively. For diamond-type crystals of Si and Ge, the forces are covalent and noncentral; the ratio of the noncentral (β) to the central (α) forces was calculated to be about $\beta/\alpha = 0.3$ by the valence-force-field model [17].

This remarkable finding of the Cauchy relation in the ice VII phase suggests that the interpenetration of two diamondlike I_c sublattices will induce central forces between each atom. Now, on the basis of our experimental results that the forces may act effectively along the line joining the atoms (central forces), we can calculate three elastic constants as a function of the force constants and investigate the force fields on C_{11}, C_{12}, and C_{44}, by using the spring force constants $\mathbf{k}_0$, $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ as shown in Fig. 1. $\mathbf{k}_0$ is for the nearest-neighbor hydrogen-bonded O—$H$$\cdots$$O$ (own 4 pairs); $\mathbf{k}_1$ is for the nearest-neighbor nonbonded ($\neq \mathbf{k}_0$) oxygen atoms (4 pairs); $\mathbf{k}_2$ is for the second-neighbor nonbonded oxygen atoms (6 pairs); and $\mathbf{k}_3$ is for the third-neighbor weakly bonded oxygen atoms (own 12 pairs). Here, $\mathbf{k}_0$ is not equal to $\mathbf{k}_1$, but is near to it, because the hydrogen bonding is weak in strength. First, we calculate the change in the internal energy of the crystal when it is distorted from its equilibrium shape. Then, we can calculate the energy stored in the springs having the force constants $\mathbf{k}_m$, which is $\mathbf{k}_m/2$ times the square of the extension for each spring:

$$\mathbf{k}_m (e_{ij}d)^2/2, \tag{4}$$

where e_{ij} is a strain component and d is the distance between each pair of atoms [18]. To get the total energy of all the springs connected to the central oxygen atom (see Fig. 1), we need the sum of 26 terms like Eq. (4). Next, by comparing the resulting expression for the total energy with the well-known macroscopic expression for cubic crystals,

$$U = C_{11}(e_{xx}^2 + e_{yy}^2 + e_{zz}^2)/2$$
$$+ C_{12}(e_{yy}e_{zz} + e_{zz}e_{xx} + e_{xx}e_{yy})$$
$$+ C_{44}(e_{yz}^2 + e_{zx}^2 + e_{xy}^2)/2, \tag{5}$$

we can identify the coefficient of each term with the elastic constants as follows:

$$C_{11} = (\mathbf{k}_0 + \mathbf{k}_1)/3a + 6\mathbf{k}_2/3a + 12\mathbf{k}_3/3a,$$
$$C_{12} = (\mathbf{k}_0 + \mathbf{k}_1)/3a + 6\mathbf{k}_3/3a, \tag{6}$$
$$C_{44} = (\mathbf{k}_0 + \mathbf{k}_1)/3a + 6\mathbf{k}_3/3a,$$

where a is the bcc lattice constant. We have been able to relate the elastic constants to the atomic properties which are characterized by the constants $\mathbf{k}_0$, $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$. Moreover, we could derive the Cauchy relationship $C_{12} = C_{44}$ which applies only for atomic interactions with central forces, based on our present experimental results. It is noted that the C_{12} and C_{44} depend on the sum of the nearest-neighbor $\mathbf{k}_0$ and $\mathbf{k}_1$, and the third-neighbor weakly bonded $\mathbf{k}_3$. By using our typical experimental results,

$C_{11} = 37.6$ GPa, $C_{12} = C_{44} = 20.8$ GPa at 2.30 GPa ($a = 3.368$ Å), we estimated $k_0 + k_1 + 6k_3 = 21.0$ N/m and $k_2 + k_3 = 2.8$ N/m. It has turned out from these results that the contribution of weakly bonded k_3 to C_{12} and C_{44} is very small, but k_0 and k_1 contribute one predominantly to them, i.e., the nearest neighbors mainly support the formation of the Cauchy relationship. Therefore the interpenetration (self-clathrate structure) of the two ice I_c sublattices can cancel the noncentral terms which exist in each diamond-type lattice. As a result, this situation can induce the central forces which are represented by the effective sum of the nearest-neighbor hydrogen-bonded k_0 and nonbonded k_1 [see Eq. (6): contributions to C_{12} and C_{44}]. This feature would result in the greatest stability of the ice VII phase under hydrostatic pressure with no amorphization; the stability might be because of central interactions acting along lines joining the centers of the atoms.

We believe that our high-pressure Brillouin experiments in cubic ice VII revealed the important property of the Cauchy relation $C_{12}(P) = C_{44}(P)$ which suggests that the atoms interact with central forces, and this significant finding will stimulate theoretical calculations which undertake to describe the high-pressure densest ices VII and VIII from "first principles."

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