Brillouin scattering from H_2O: Liquid, ice VI, and ice VII

A. Polian

Laboratoire de Physique des Milieux Très Condensés, Université Pierre et Marie Curie,
4 Place Jussieu, F-75230 Paris Cedex 05, France

M. Grimsditch

Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439
(Received 22 December 1982)

Brillouin scattering from H_2O under hydrostatic pressures up to 30 GPa is reported. Sound velocities in the liquid region agree with previous ultrasonic measurements and discontinuities are observed at the liquid—ice VI and ice VI—ice VII phase transitions. Elastic moduli derived from the frequency shifts are compared with bulk modulus values obtained from compressibility data.

INTRODUCTION

There are now nine known phases of solid H_2O labeled[1] ice I through ice IX. Of these, ice I occurs in both cubic and hexagonal form and ice VI is thought to exist in tetragonal and orthorhombic forms. Although the existence of all these forms of ice is known, surprisingly little is known about their general physical properties due to the difficulties involved in high-pressure experiments. Recent advances in Fabry-Perot interferometry techniques[2] have now made it possible to perform Brillouin scattering experiments from samples inside diamond-anvil pressure cells.[3-6]

In this study, we have used Brillouin scattering to study H_2O at room temperature in the range 0—30 GPa. Using published density results and making certain assumptions for the refractive index variation with pressure, we obtain values for elastic moduli which are compared with the bulk modulus obtained from density measurements. The elastic constants are also analyzed in the context of Murnaghan's equation of state.

EXPERIMENTAL

The diamond-anvil cell used in these experiments is described in Ref. 7. This type of construction, contrary to that used in Refs. 3 and 5, only allows experiments to be done in the backscattering geometry and consequently suffers from the drawback that the refractive index is needed in order to interpret the results. It also only allows information to be obtained on the velocity of longitudinal waves. The big advantage of this construction is, however, that considerably larger stresses can be obtained. Furthermore, we shall show that in this case uncer-

tainties in the refractive index lead only to small corrections.

The Brillouin spectra were taken with a five-pass Fabry-Perot interferometer using ~120 mW of 515-nm radiation from a single-moded Ar-ion laser. Some of our measurements on ice VI were done on single crystals. These can be obtained from the polycrystalline phase (normally obtained by increasing the pressure) by slowly decreasing the pressure to obtain ice VI in equilibrium with water. Careful changes in pressure can then be made until a single crystal of ice VI is left. Subsequent pressure increase then yields a single large crystal. We have not measured the crystallographic orientation of these crystals: However, they are birefringent and the pattern produced by the facets of the crystal when a laser beam is transmitted through the cell (the pattern showed two mirror planes at 90°) indicates that either a [100] or a [110] axis is along the cell axis.

The pressure in the cell was measured, using the ruby calibration, before and after each spectrum was taken. The reproducibility of the readings is found to be ~0.05 GPa.

RESULTS AND DISCUSSION

The observed Brillouin frequency shifts Δv, due to longitudinal phonons, are shown in Figs. 1 and 2 as a function of pressure P. These frequency shifts are related to the sound velocity V through

$$\Delta v = 2nV/c\lambda, \tag{1}$$

where c is the velocity of light, λ the wavelength of the incident radiation, and n is the refractive index. Using Eq. (1) we have calculated nV which is given on the right-hand sides of Figs. 1 and 2.
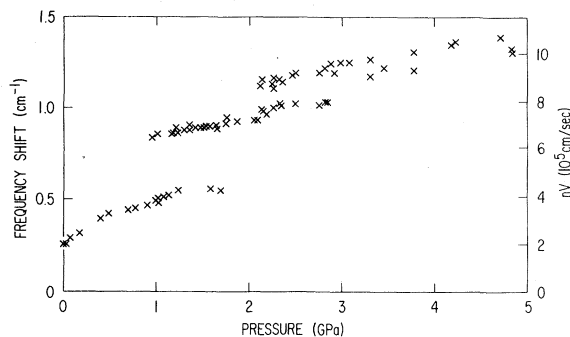
FIG. 1. Brillouin frequency shift and the product, nV, of the various room-temperature phases of H_2O up to 5 GPa.

In order to interpret and discuss the data of Figs. 1 and 2 we need the pressure dependence of the density and of the refractive index. The density of the various H_2O forms as a function of pressure has already been measured[8-11] and is shown in Fig. 3 for pressures up to 8 GPa. The refractive index of liquid H_2O is known up to 1.1 GPa.[12] We have measured the refractive index of ice VI in equilibrium with water by the following method: When water and a single crystal of ice VI coexist in the cell, we measure the interference fringes in the transmission spectrum of water; because the refractive index is known the distance between the diamond faces can be evaluated. We then measure the interference fringes through the ice-VI crystal and obtain its refractive index. At 1.05 GPa the refractive indices are the following: 1.415 for water and 1.444 for ice VI. To obtain the refractive index at higher pressures in ice IV and ice VII we recall that the changes in refractive index have been shown[12] to be well
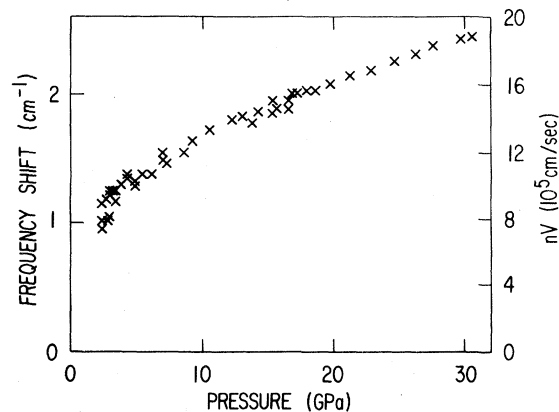
described by a linear function of Eulerian strain, i.e.,

$$n(\rho_0) - n(\rho) = A\epsilon , \tag{2}$$

where ρ is the density, A is a constant, and

$$\epsilon = \frac{1}{2}\left[1 - \left[\frac{\rho}{\rho_0}\right]^{2/3} \right] . \tag{3}$$

We have fitted expression (2) in the liquid region and then extrapolated (through the two-phase transitions) to ice VI and ice VII with the same value of $A = 1.02$. This extrapolation is shown in Fig. 3. In ice VI at 1.05 GPa the measured and extrapolated values agree to within 1%.

It is remarkable that this extrapolation, taking into account only the density variation, produces such good results. However, the fact that H_2O retains its molecular character in all its observed solid forms explains this result and allows us to use the same extrapolation into the ice-VII phase and at higher pressures. We point out however that an ionic phase has been predicted to exist[13] in the 50—100-GPa range in which the above assumptions could not be expected to hold.

We now make the following points with the results of Figs. 1 and 2. (i) The sound velocity in the liquid region ($P \lesssim 1$ GPa) obtained by using our frequency shifts and the refractive index data of Ref. 12 agrees within experimental error ($\sim 2\%$) with the ultrasonic values of Ref. 14. (ii) It was often the case that on increasing the pressure, ice VI would not be produced at ~ 1 GPa but at higher values. This can be seen by the points above 1 GPa that lie on the continuation of the liquid results. When the transition occurs (as has been previously reported) it is seen as a "flash" when observed through a microscope. (iii) Using $V = (C_{11}/\rho)^{1/2}$ and the values of ρ from Fig. 3, we find for the liquid
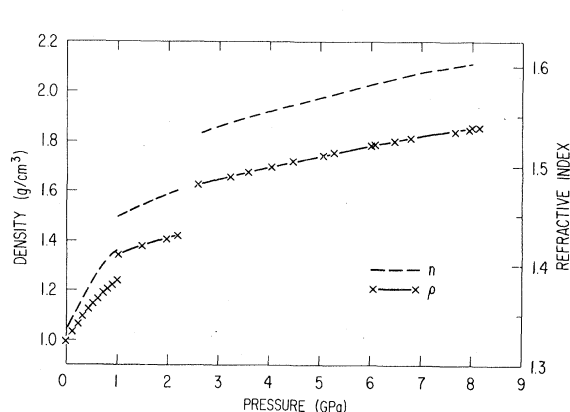

FIG. 2. Same as Fig. 1 in the ice-VII phase up to 30 GPa.

FIG. 3. Refractive index and density of H_2O vs pressure.

$C_{11}(P=0)=2.2\pm0.1$ and $C_{11}(P=1$ GPa$)=9.2\pm0.4$ GPa. These values are consistent with the bulk modulus B (which for a liquid is equal to C_{11}) determined from density variations,[8] i.e., $B(P=0)=2.4\pm0.1$ and $B(P=1$ GPa$)=8.3\pm1.0$ GPa. (iv) The frequency shifts observed in ice VI, which is known to be either tetragonal or orthorhombic, were independent of whether we were dealing with a single crystal or a polycrystalline sample. This points to ice VI being elastically isotropic. However, all the single crystals of ice VI in equilibrium with liquid obtained by the method outlined in the preceding section showed a characteristic diffraction pattern when illuminated by a laser beam. This pattern is produced by the naturally occurring crystallographic faces and was the same for all samples indicating identical orientation. Hence it is conceivable that because of the manner in which pressure is applied we always investigate the same direction of phonon propagation. (v) The fact that ice-VI single crystals are birefringent, enabled us to record spectra with the incident light polarized parallel and perpendicular to the crystal axes. We found no change ($<1\%$) in the position of the Brillouin lines indicating that the birefringence of ice VI is small (i.e., $<1\%$). This is also known to be true for ice Ih.[15] (vi) Defining $V=(C/\rho)^{1/2}$ where C is some combination of the elastic moduli, we obtain for ice VI: $C(P=1$ GPa$)=28$ GPa and $C(P=2$ GPa$)=34$ GPa. The mean value of the bulk modulus determined from the density over this region is $B=21\pm1$ GPa. If we assume that ice VI is elastically isotropic then $C=C_{11}$ and $B=C_{11}-\frac{4}{3}C_{44}$ and the fact that $B<C$ is not surprising. (vii) In the ice-VII (cubic) phase the position of the peaks at a given pressure changes when the sample is taken into the liquid form and then resolidified as shown in Figs. 1 and 2. Furthermore, in one particular run two peaks were observed and followed as a function of pressure indicating that the volume sampled contained two crystallites. We interpret these variations as an indication of elastic anisotropy. Figure 2 shows that this anisotropy in the velocities of longitudinal phonons in ice VII close to the phase transition is around 10% and tends to decrease at higher pressures. (viii) The effective elastic modulus C for longitudinal waves in ice VII can be calculated to be 57, 106, 166, and 279 GPa at pressures of 3, 8, 15, and 30 GPa, respectively. The values of the bulk modulus obtained from the density measurements[11] at these pressures are 28, 49, 77, and 139 GPa, respectively. The larger differences between B and C in ice VII than in ice VI and the increase of this difference with pressure is an indication of a substantial increase of the shear wave velocity in ice VII over that in ice VI, and of the in-
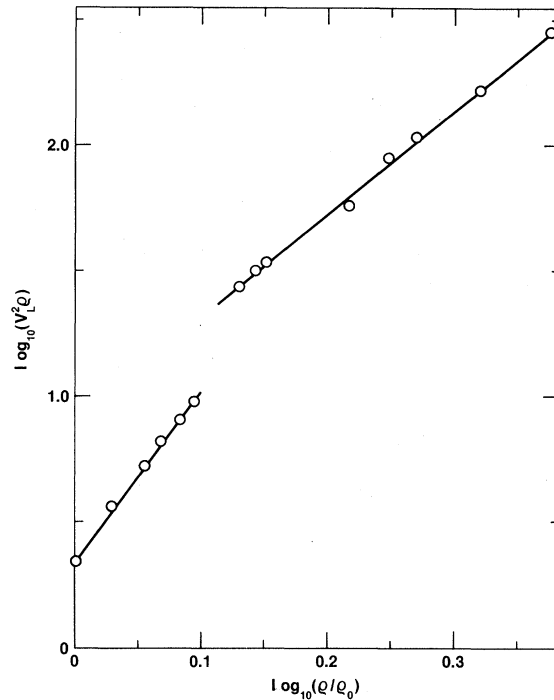

FIG. 4. Plot of $\log_{10}(V_L^2\rho)$ vs $\log_{10}(\rho/\rho_0)$ for H$_2$O at room temperature.

crease in shear elastic modulus versus pressure in ice VII. This is consistent with the rigid structure of ice VII, i.e., two interpenetrating face-centered-cubic sublattices. (ix) We have chosen to analyze our elastic moduli data in terms of Murnaghan's equation of state. In Fig. 4, we plot the logarithm of our calculated values of C vs $\log_{10}(\rho/\rho_0)$. As can be seen, the liquid region [$\log_{10}(\rho/\rho_0)<0.1$] is well approximated by a straight line of slope 6.8 and both the ice VI and VII regions appear to be roughly on the same line with a slope of 4.3.

The value of the slope in the liquid region is to be compared with the slope found for a methanol-ethanol mixture[4] 7.1 and also that calculated on the basis of a Lennard-Jones potential which yields 7.0. The good agreement indicates that the intermolecular forces in liquid H$_2$O are probably well described by van der Waals–type forces.

In the solid region however, Fig. 4 shows that the nature of the forces has changed compared to that in the liquid state. This is consistent with the fact that hydrogen bonding plays an important role in describing the forces between water molecules in the solid state. Our measured value of the slope (C') of the plot of $\log_{10}C$ vs $\log_{10}\rho$ in ices VI and VII (i.e., $C'=4.3$) is consistent with the value found in Ref. 11 from the plot of $\log_{10}B$ vs $\log_{10}\rho$ (i.e., $B'=dB/dP=4.11$). This value of B' is similar to those in most crystals. In particular, using the

values of the pressure dependence of the elastic moduli,[16] we obtain $C' = 2.4$ and $B' = 4.5$ for ice Ih.

In summary we have shown that Brillouin scattering is an effective tool for the study of the elastic properties of the various high-pressure phases of H_2O at room temperature. We have determined the longitudinal sound velocity in the liquid, ice-VI, and ice-VII phases. The volume dependence of the velocities in ice VI and VII are similar and not far from the value previously found for ice Ih; they differ however from that in the liquid. We have also observed an elastic anisotropy in the (cubic) ice-VII phase which decreases with increasing pressure.

ACKNOWLEDGMENTS

[1]See, for example, B. Kamb, in *Physics and Chemistry of Ice,* edited by E. Whalley, S. Jones, and L. Gold (Royal Society of Canada, Ottawa, 1973), p. 29.

[2]J. R. Sandercock, in *Light Scattering from Solids,* edited by M. Balkanski (Flammaion, Paris, 1971), p. 9.

[3]C. H. Whitfield, E. M. Brody, and W. A. Bassett, Rev. Sci. Instrum. <u>47</u>, 942 (1976).

[4]A. Polian, J. M. Besson, M. Grimsditch, and H. Vogt, Appl. Phys. Lett. <u>38</u>, 334 (1981).

[5]H. Shimizu, E. M. Brody, H. K. Mao, and P. M. Bell, Phys. Rev. Lett. <u>47</u>, 128 (1981).

[6]A. Polian, J. M. Besson, M. Grimsditch, and H. Vogt, Phys. Rev. B <u>25</u>, 2767 (1982).

[7]G. J. Piermarini and S. Block, Rev. Sci. Instrum. <u>46</u>, 973 (1975).

[8]G. Kennedy and W. Holser, in *Handbook of Physical Constants,* edited by S. P. Clark (Geological Society of America, New York, 1966), p. 371.

[9]P. W. Bridgman, Proc. Am. Acad. Arts Sci. <u>74</u>, 399 (1942).

[10]B. Olinger and P. Halleck, J. Chem. Phys. <u>62</u>, 94 (1975).

[11]R. G. Munro, S. Block, F. A. Mauer, and G. Piermarini, J. Appl. Phys. <u>53</u>, 6174 (1982).

[12]K. Vedam and P. Limsuwan, J. Chem. Phys. <u>69</u>, 4762 (1978).

[13]F. H. Stillinger and K. S. Scheizer in Proceedings of the Sixth International Symposium on Physics and Chemistry of Ice, University of Missouri, Rolla, 1982 (unpublished); G. E. Walrafen, M. Abebe, F. A. Mauer, S. Block, G. L. Piermarini, and R. Munro, J. Chem. Phys. <u>77</u>, 2166 (1982).

[14]G. Holton, J. Appl. Phys. <u>22</u>, 1407 (1951).

[15]H. E. Merwin, Int. Crit. Tabl. <u>7</u>, 16 (1930).

[16]B. Brockamp and H. Rüter, Z. Geophys. <u>35</u>, 277 (1969).