

New High-Pressure Phase of H₂O: Ice X

A. Polian

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

and

M. Grimsditch

Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 7 October 1983)

H₂O at 300 K has been studied up to 67 GPa by Brillouin scattering. A transition to a new form of ice occurs at 44 GPa. This is the tenth known solid form of H₂O and may be the expected "symmetric-ice" structure.

PACS numbers: 62.50.+p, 64.30.+t, 78.35.+c

A study of the phase diagram of H₂O, which contains nine solid phases,¹ clearly evidences the fascinating complexity of this substance. All of the nine known solid phases consist of well defined H₂O molecules bonded by relatively weak hydrogen bonds. However, as early as 1972 Holzappel² predicted that **a high-pressure phase of H₂O should exist in which the H₂O molecule was no longer the basic building block, but a structure in which each oxygen atom would share its hydrogen with neighboring oxygen atoms. This structure, called symmetric ice, was predicted to form between 35 and 50 GPa.**

A later calculation by Stillinger and Schweizer³ indicated that this phase would be ionic in nature and would be formed at pressures between 50 and 100 GPa. A more recent study by the same authors⁴ indicates that the transition is at 45 GPa. The predicted increase in the ionicity of the OH bond at high pressures has recently been reported by Klug and Whalley⁵ in infrared absorption experiments up to 19 GPa.

The fact that pressures above 50 GPa are now achievable with diamond anvil cells has led to some effort to identify this high-pressure phase of H₂O. Recent infrared absorption measurements up to 14 GPa by Holzappel, Seiler, and Nicol⁶ indicate that the frequencies of the $\nu_R E_\mu^3$ and $\nu_2 A_{2\mu}^1$ modes, which are expected to be degenerate in the symmetric phase, extrapolate to a crossing at ~ 25 GPa. Raman-scattering results obtained very recently by Hirsch and Holzappel⁷ at 100 K show a broadening followed by the disappearance of the OH stretch mode at ~ 50 GPa and the appearance of a new mode at ~ 38 GPa. These results are found to be consistent with the formation of symmetric ice in the presence of large stress inhomogeneities.

In a recent article we reported results of a Brillouin scattering study up to 30 GPa⁸ in which no anomalous behavior was observed. In this paper we present an extension of those results up to 67 GPa. An anomaly in the behavior of the longitudinal sound velocity is found at 44 ± 2 GPa indicating that a phase transition has occurred. Brillouin scattering does not enable us to determine if it is indeed the expected symmetric ice form, since it could equally well be an ionic OH⁻-OH₃⁺ phase which has also been proposed.⁴

The pressure cell used in these experiments was constructed following the design of Mao *et al.*⁹ This type of cell allows experiments to be performed only in the backscattering geometry and has an aperture of only 6×10^{-2} sr. In order for the Brillouin signal to be observable above the very intense scattered stray laser radiation it was necessary to use a tandem 5 + 2 Fabry-Perot interferometer.¹⁰ The spectra were recorded with use of 515-nm radiation from a single-mode Ar laser with powers ranging from 50 to 300 mW. The experiments were performed at room temperature and the H₂O sample transformed at 0.9 GPa to ice VI and to ice VII at 2 GPa. The pressure was determined with the linear ruby fluorescence scale¹¹ (i.e., $-7.53 \text{ cm}^{-1} / \text{GPa}$).

In Fig. 1 we present our results for the measured Brillouin frequency shift from longitudinal phonons as a function of pressure. Below 30 GPa they agree with our previous results⁸ and as explained there the measured frequency shift is directly proportional to nV , where n is the refractive index and V the velocity of longitudinal sound waves; nV is given on the right-hand side of Fig. 1. Above ~ 40 GPa the ν versus P curve clearly deviates from its low-pressure behavior. As a result of the nonlinear behavior of the results shown in Fig. 1 it is difficult

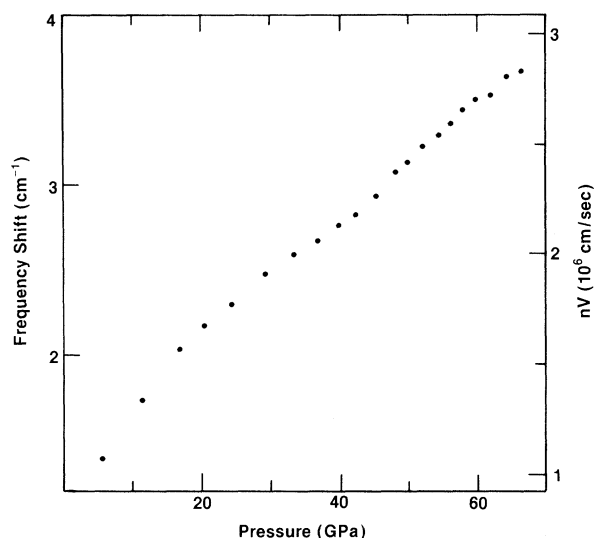


FIG. 1. Measured Brillouin frequency shift from longitudinal sound waves in H₂O as a function of pressure.

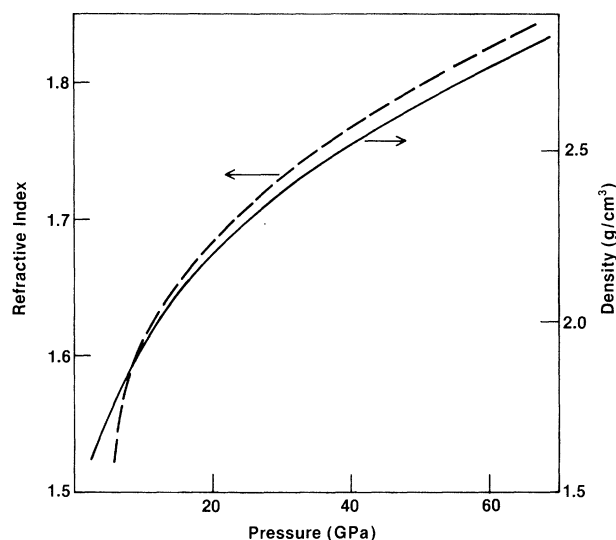


FIG. 2. Extrapolated values of density (Ref. 12) and refractive index as a function of pressure.

to establish exactly at what pressure the change takes place.

In order to establish unambiguously the existence of a phase transition we have analyzed our results in the same manner as was done in Ref. 8. Since to do this requires knowledge of both the density and refractive index it has been necessary to extrapolate them up to 67 GPa. We perform the extrapolation assuming that no phase transition occurs and hence that both density (ρ) and refractive index must be monotonic and smoothly varying functions of the pressure (P). If no phase transition occurs we expect the behavior of the elastic constant C also to be monotonic and smoothly varying. Any deviation from this behavior would indicate the presence of a phase transition. The density was extrapolated by fitting the function

$$P = P_0 + P_1\rho + P_2\rho^2 + P_3\rho^3, \quad (1)$$

(where P_0 – P_3 are adjustable parameters) to the data of Munro *et al.*¹² who have measured the density up to 36 GPa. Our fit yields $P_0 = -40.27$, $P_1 = 70.85$, $P_2 = -48.33$, and $P_3 = +13.03$. The refractive index is extrapolated as in Ref. 8, i.e.,

$$n = 1.334 + 0.51(\rho^{2/3} - 1). \quad (2)$$

The values of the density and refractive index thus obtained are shown in Fig. 2. We mention that we also calculated the density by extrapolating the bulk modulus determined in Ref. 12 by using

$$B = B_0 + B_1P + B_2P^2 + B_3P^3 \quad (3)$$

and then using

$$\ln(\rho/\rho_0) = \int_{P_0}^P B^{-1} dP. \quad (4)$$

The differences between the two density extrapolations are small and do not noticeably affect the following analysis.

Using nV from Fig. 1 and n and ρ from our extrapolations we calculate

$$C = V^2\rho, \quad (5)$$

where C is an effective longitudinal elastic modulus. In Fig. 3 we plot $\log C$ (C in gigapascals) vs $\log(\rho/\rho_0)$ (where ρ_0 is the density of liquid H₂O at 1 bar and room temperature). In this plot a very evident break in the linear behavior is observed at ~ 44 GPa. We have performed linear least-squares fits to the data above and below $\log_{10}(\rho/\rho_0) = 0.41$. The slope below this value is 4.1 in good agreement with the value 4.3 determined in Ref. 8. Above $\log_{10}(\rho/\rho_0) = 0.41$ the slope is 6.0. We interpret this discontinuity in the slope as evidence of a phase transition at 44 ± 2 GPa. We stress that the calculated values of C in the high-pressure phase are necessarily incorrect since the calculation utilizes extrapolated values of n and ρ . Furthermore although the discontinuity in C could be eliminated by appropriate changes in n or ρ , it would then be the discontinuities in either dn/dP or $d\rho/dP$ that would imply a phase transition.

The phase above 44 GPa is the tenth known solid phase of H₂O and, for reasons given earlier, is probably the predicted²⁻⁴ symmetric ice. As such it

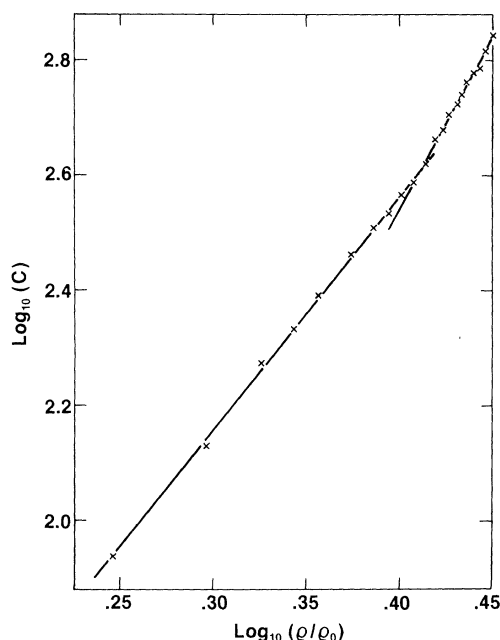


FIG. 3. Logarithm of the effective longitudinal elastic modulus (expressed in gigapascals) vs the logarithm of the density. The straight lines are least-squares fits to the data above and below $\log_{10}(\rho/\rho_0) = 0.41$.

would be the first nonmolecular structure for H_2O . Within the accuracy of our measurements the observed transition is not first order; however, we cannot rule out the possibility that pressure inhomogeneities (estimated to be ~ 6 GPa from the width of the ruby fluorescence) could in effect smear out a first-order transition and make it look like a higher-order transition.

In the high-pressure phase the band edge was still above ~ 3 eV as ascertained by visually observing the transmission through the sample.

We mention that if instead of the linear ruby pressure scale the nonlinear scale¹³ is used, we obtain¹⁴ 4.1 and 5.4 for the slopes in the ice VII and X phases, respectively, the transition pressure at 49 GPa, and the highest pressure attained as 74 GPa.

We wish to thank Dr. M. Besson, Dr. W. Holzapfel, Dr. M. Nicol, and Dr. G. Piermarini for helpful discussions and Dr. M. Besson, Dr. A. Rahman, and Dr. J. Jorgensen for a critical reading of the manuscript. This work has been supported by the U. S. Department of Energy, the Institut National d'Astronomie et de Geophysique under Grant No. 83-070978, and the Direction des Recherches, Etudes et Techniques under Grant No. 80-500.

¹See, for example, B. Kamb, in *Physics and Chemistry of Ice*, edited by E. Whalley, S. J. Jones, and L. W. Gold (Royal Society of Canada, Ottawa, 1973), p. 28.

²W. B. Holzapfel, *J. Chem. Phys.* **56**, 712 (1972).

³F. H. Stillinger and K. S. Schweizer, in *Proceedings of the Sixth International Symposium on the Physics and Chemistry of Ice*, University of Missouri-Rolla, August 1982 (to be published).

⁴K. S. Schweizer and F. H. Stillinger, *J. Chem. Phys.* **80**, 1230 (1984).

⁵D. D. Klug and E. Whalley, in *Proceedings of the Ninth International High Pressure Conference*, Albany, New York, 1983 (to be published).

⁶W. B. Holzapfel, B. Seiler, and M. Nicol, to be published.

⁷R. Hirsch and W. B. Holzapfel, private communication.

⁸A. Polian and M. Grimsditch, *Phys. Rev. B* **27**, 6409 (1983).

⁹H. K. Mao, P. M. Bell, K. J. Dunn, R. M. Chrenko, and R. C. DeVries, *Rev. Sci. Instrum.* **50**, 1002 (1979).

¹⁰J. R. Sandercock, in *Topics in Applied Physics*, edited by M. Cardona and G. Güntherodt (Springer-Verlag, Berlin, 1982), Vol. 51, p. 173.

¹¹See, for example, A. Jayaraman, *Rev. Mod. Phys.* **55**, 65 (1983).

¹²R. G. Munro, S. Block, F. A. Mauer, and G. Piermarini, *J. Appl. Phys.* **53**, 6174 (1982).

¹³H. K. Mao and P. M. Bell, *Science* **200**, 1145 (1978).

¹⁴A. Polian, J. M. Besson, and M. Grimsditch, in *Proceedings of the International Symposium on Solid State Physics Under Pressure*, Izv. Nagaoka-Spa, Japan, January 1984 (to be published).