ACOUSTIC VELOCITIES IN ICE Ih, II, III, V AND VI, BY BRILLOUIN SPECTROSCOPY

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Résumé – La spectroscopie Brillouin à haute résolution a été employée pour déterminer les vitesses acoustiques longitudinales et transversales dans des aggrégats polycristallins isotropes de glace I_h, II, III, V et VI. Les données peuvent être expliquées au moyen d'un schéma classique basé sur la liaison hydrogène. Les modules de compressibilité (- 5%) obtenus à partir des données de vitesse pour la glace II, III, V et VI sont 138.9, 98.7, 141.9 et 181.4 kbar respectivement. La densité a aussi été mesurée au moyen d'une nouvelle technique.

Abstract
    The technique of high resolution Brillouin spectroscopy has been used to determine longitudinal and transverse acoustic velocities in isotropic polycrystalline aggregates of ice Ih, II, III, V and VI. The data can be explained on the basis of a classification scheme, founded on knowledge of hydrogen-bonding. The bulk moduli (±5%) derived from the velocity data, for ice II, III, V and VI are 138.9, 98.7, 141.9, and 181.4 kbar respectively. Also, the density has been measured using a new technique.

Introduction

    Since the most complete hydrogen-bonded materials are probably the various solid crystalline phases of water, these substances are ideally suited to studies, including the elastic properties, which provide information which can be used to refine hydrogen-binding models of the water-water interaction, for example [1-4]. Ice studies are also important because of recent discoveries of extraterrestrial H_2O, which exists in low temperature and/or high pressure environments elsewhere in the solar system, reviewed in refs. [5-6].

Experimental Technique

    The technique of Brillouin spectroscopy is discussed in the previous paper and details of the light scattering setup, data aquisition system and high pressure cell are referred to there.
    The Brillouin equation requires a knowledge of the refractive index of the scattering medium. The method of refs. [7-8] was used to obtain the refractive indices from densities. Reliable density data was needed for this analysis.
    Essentially the technique used to determine the density involved measuring the amount of compression that an ice sample experienced when hydrostatic pressure was applied to it. A sample, cut from a single crystal of Mendenhall glacial ice, was confined within a thick-walled stainless steel cylindrical chamber (Figure 1), inside the high pressure cell. One end was sealed and the other end was open so that any pressure induced change in the sample's volume was translated into a change in its length, by extrusion, since its diameter remained fixed, ie. $\Delta V/V = \Delta L/L$, where V is volume and L is the length of the sample. ΔL was measured by recording the movement of a glass plug which was frozen to the end of the ice specimen.

All of the density data were very consistent and exhibited abrupt discontinuities at each of the phase transformations (Figure 2). The data for the various ice phases was least-squares fitted with either linear or quadratic expressions, depending on whether curvature was obvious in the data plots, and are given below.

$$\rho_{iceIh}(P) = .9228 + 7.2785 \times 10^{-3}P + 7.5023 \times 10^{-4}P^2$$

$$\rho_{iceII}(P) = 1.1698 + 8.1760 \times 10^{-3}P$$

$$\rho_{iceIII}(P) = 1.1321 + 1.2057 \times 10^{-2}P \qquad\qquad (1)$$

$$\rho_{iceV}(P) = 1.1974 + 1.9632 \times 10^{-2}P - 1.0982 \times 10^{-3}P^2$$

$$\rho_{iceVI}(P) = 1.1559 + 4.5212 \times 10^{-2}P - 2.4345 \times 10^{-3}P^2$$

In the above expressions ρ denotes density in g/cm^3 and P denotes pressure in kbar.
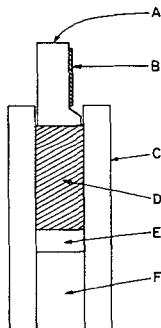

Figure 1. Density determination apparatus: A, right cylindrical glass plug; B, scale with .1 mm markings; C, thick - walled stainless steel tube; D, ice sample; E, hard soldered stainless steel plug; F, coupling space for mounting onto stem inside the high pressure cell.
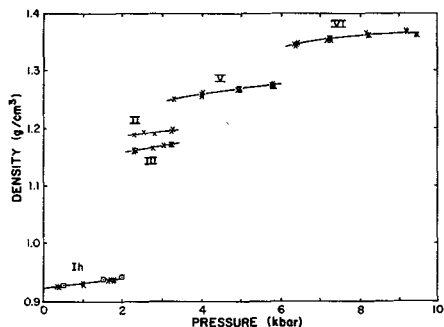
Figure 2. Density vs. pressure for the various ice phases. The solid lines represent least-squares fits to the data points shown as x's. The boxed points in the data for ice Ih are densities determined from the bulk moduli of the previous paper. All points were obtained at -35.5°C.

By rapidly freezing vigorously boiled deionised water, samples of bubble free, polycrystalline aggregates of very small, and uniform crystallites, were produced for the light scattering experiments. To prevent ice samples from grossly deforming during phase transformations it was necessary to partially confine them in a glass cell (Figure 3) which would allow them to expand and contract lengthwise, and yet preserve their cylindrical shape.

Five different specimens were used in the light scattering work. Most of the Brillouin experiments were conducted at a temperature of -35.5°C, except for ice III, which were conducted at -27.2°C. A typical averaged data point was obtained by setting the pressure at a desired value within the stability region of a given phase, and then running a set of eight different Brillouin scattering experiments at evenly spaced sample rotation settings, fully spanning 360°. These were then averaged and the result was assumed to be a reasonable estimate for the acoustic velocity in homogeneous polycrystalline ice of that particular phase, at that pressure. This approach was verified by obtaining averaged frequency shifts for three different polycrystalline samples of ice Ih at zero pressure, and comparing the values with those calculated from an averaging procedure using the elastic constants of ice Ih (see previous paper). The experimental results were in excellent agreement, within .3%, with the calculated value. The transverse frequency shift components, which were characteristically much weaker than the longitudinal components, were often

lost in the background noise so that averaged transverse shifts were not obtained at each pressure setting and are therefore presented as single data point values. The uncertainties associated with the measured frequency shifts of longitudinal and transverse components, for any particular Brillouin scattering experiment, were typically ±1.5% and ±3.5% respectively. The standard deviations in the longitudinal measurements for ice II, III, V and VI were ±2.3%, ±2.8%, ±2% and ±1.5% respectively. Hence, ice VI appeared to be the most isotropic of the ices.
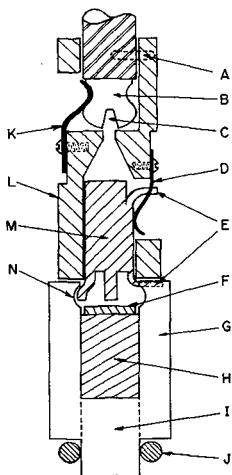

Figure 3. Glass cell and brass sample holder for Brillouin scattering experiments : A, securing pin; B, rotation stem head; C, darkened hole to minimize laser backscatter; D, retaining clip; E, anti-rotation fingers; F, glass disc to minimize oil inclusion during phase transitions; G, thick pyrex tube; H, polycrystalline ice sample; I, right cylindrical pyrex plug with polished flattened ends, fused to glass tube; J, copper ring for gripping the glass cell; K, retaining clip; L, brass sample holder; M, tubular brass coupler; N, niche to secure the brass coupler to the glass cell.

Results and Analysis

Upon examination of the data in Figure 4 the most striking feature is the drop in longitudinal velocity in ice III compared with ice Ih, though the density increased by ~20%. Also the velocity of ice II is high relative to that of ice III and ice V, though the density of ice II was only slightly higher than ice III and less than ice V. In the efforts made to explain these, and other general features, the following picture, based on strengths of the hydrogen bonds, emerged.

Three classes serve to distinguish the five ices studied here. Class 1 encompasses those ices which are proton disordered with linear hydrogen bonds. Ice Ih belongs to this class. The ices III, V and VI belong to Class 2, which are disordered ices with O-H...O bonds that deviate from linearity by comparable degrees. Class 3 contains proton ordered ices which have nonlinear hydrogen bonds. Ice II belongs to Class 3. Linear hydrogen bonds are stronger than bent ones of comparable length, and so are proton-ordered bonds as compared to disordered ones.

Based on the results of ultrasonic experiments on various rocks, it has been suggested [9] that the density and velocity of compressional waves are linearly related for solids of constant mean atomic weight. Results from the previous paper confirmed this for ice Ih. The velocity data [10] for ice III, and ice V, also separately verified the hypothesis. The longitudinal velocities from the present work, corresponding to the pressure at the midpoints of the three sets of density data for the ices III, V and VI, which are Class 2 ices, were plotted against the associated densities, and again, a good fit was obtained (Figure 5). The velocity of ice II, a Class 3 phase, lies above the velocity-density line of Class 2 ices because it is proton ordered. Ice Ih, which is a disordered phase belonging to Class 1, has linear hydrogen bonds which are the shortest of any phase, and consequently its longitudinal velocity lies well above the velocity-density line of ices III, V and VI. Ice VII is a disorderd phase, with O-H...O bonds that are linear. This puts it in Class 1, however, some distinction has to be made between this ice and ice Ih because the hydrogen bonds of ice Ih are short. Class 1_a refers to disordered ices

with short linear bonds, such as ice Ih, and Class 1_b refers to disordered ices
which have moderate-to-long linear bonds, such as ice VII. The velocity of ice
VII [7], as expected, lies above the velocity-density line of the Class 2
ices, even though the studies were performed at a temperature which was 55°C
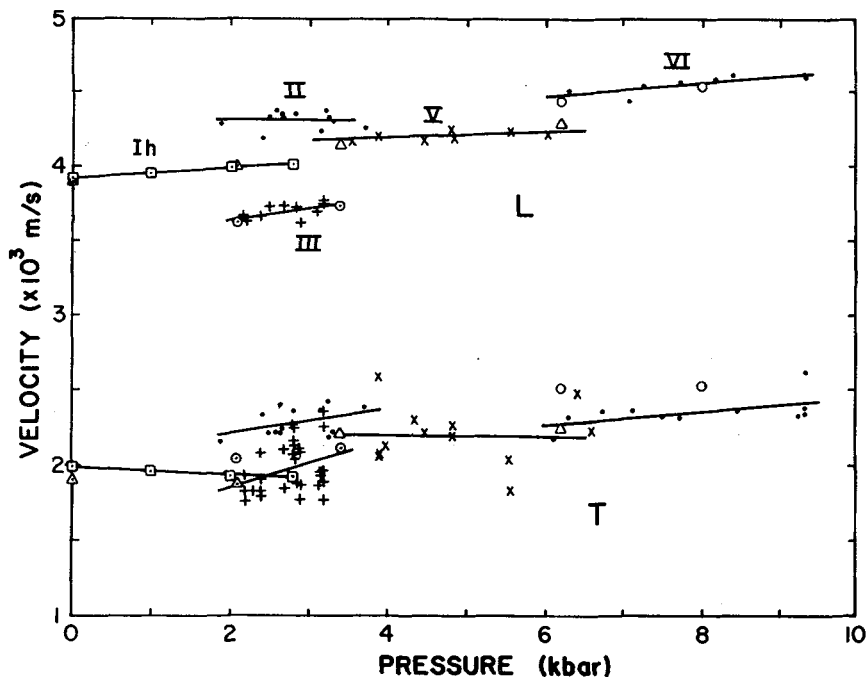higher than the present work.

Figure 4. Acoustic velocities vs. pressure for the various ice phases.
L and T designate longitudinal (averaged) and transverse (single-point)
velocities. The solid lines represent linear least-squares fits to the
data (x's, dots and crosses) for each high pressure phase. Circles and
triangles represent data from [10] at -25°C. The boxed data points and
best-fit curves shown for ice Ih were obtained from the elastic
constants of the previous paper. All of the present velocity data was
obtained at -35.5°C, except for ice III, which was obtained at -27.2°C.

Figure 5. Averaged
longitudinal velocity vs.
density for the various ice
phases. The solid line
represents a linear
least-squares fit to the
velocities of the Class 2
ices. The data point for ice
VII was obtained by [7] at
~20°C. The velocity for ice
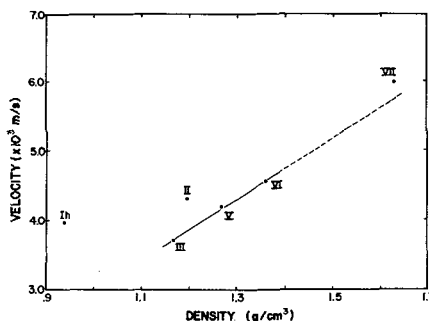Ih was taken from the
previous paper.

Table I gives the classification of most known ice polymorphs and rank, from
highest to lowest velocity, of each classification assuming that the velocity-

density slopes of the different classes are similar. No other velocity data exists for other ice phases, however, there are thermal conductivity data for several polymorphs [9] which can be used to test the classification scheme. If the product of the heat capacity and phonon mean free path do not change significantly, or vary proportionally with phonon velocity, from phase to phase, the thermal conductivity should faithfully reflect the qualitative features, at least, of the pattern of longitudinal velocities exhibited by the different phases. There is a remarkable correspondence between the thermal conductivity versus density data (extrapolated to ~250 K) [11] and the present velocity data (plus the other value [7] for ice VII). The conductivities of the Class 2 ices III, V and VI fall nearly on a straight line. Ice VII is above this line. Furthermore, ice VIII, which belongs to yet another class of structures, those which are proton ordered with linear hydrogen bonds, designated as Class 4, consequently lies well above the Class 2 line. Ice Ic belongs to Class 1_a with ice Ih. They have comparable conductivities, because of similar densities, and lie well above the conductivity-density line of the Class 2 ices. Ice IX is a Class 3 ice like ice II, but with a slightly lower density, and so has a thermal conductivity above the Class 2 line and below ice II. Each of these observations is consistent with the classification scheme.

TABLE I: ICE CLASSIFICATION AND RANK

Class	Rank	Ice Phases
1_a	1	Ih, Ic
1_b	2	VII
2	3	III, IV, V, VI
3	2	II, IX
4	1	VIII

The fact that the thermal conductivity of ice VIII lies well above that of ice VII, where the only difference according to the classification scheme is that one is ordered and the other is not, and ice II is only moderately higher than ice III for the same reason, may imply that proton ordering has a more dramatic effect, on acoustic velocities and thermal conductivity, in ices that have linear hydrogen bonds.

The value for the compressional wave velocity of ice VI [7], using Brillouin spectroscopy, was in good agreement with the present result. Recently, ultrasonic studies have been conducted [10] on ices Ih, III, V and VI for polycrystalline aggregates at -25°C. For comparison, some of this data has been included in the graphic depiction of the present velocity data (Figure 4). The degree of scatter in the present transverse velocities for any phase would seem to imply that the full range of possible values was adequately represented and fairly uniformly distributed about the least-squares lines, so that the averaged velocities taken near the midpoints of the lines, at least, are very likely free of bias. Longitudinal acoustic velocities [10] fall within ~1% of the averaged values determined for the various ices in this work. There was some disagreement, however, between the two sets of transverse data.

Tables II and III represent a synopsis of the present data, and how it compares with linearly interpolated values from [10]. The adiabatic (constant entropy) bulk modulus, B^S, for both sets of data was calculated from the density, and longitudinal and transverse velocities. The isothermal bulk modulus, B^T, for the present work was calculated from the measured densities. The adiabatic shear modulus was calculated from the density and transverse velocity. The pressures at which the calculations were carried out, quoted in the tables, correspond to the pressures at the midpoints of the density data sets for ice II, III, V and VI. The pressure associated with ice Ih is the average of the pressures which were used during the determination of the elastic constants (see previous paper).

The consistency of the present results obtained using the density data, as compared with that using the velocity data, is impressive. The two methods yield bulk moduli that agree to within 5% for all ices studied. Except for ice VI, there is reasonable agreement with the results of [10].

TABLE II: SYNOPSIS OF RESULTS FROM THE DIFFERENT ICE PHASES

Phase	Pressure (kbar)	Average Velocity (km/s)		Bulk Modulus (kbar)		Average Velocity* (km/s)		Bulk Modulus* (kbar)
	P	$\bar{V}_L$	$\bar{V}_T$	B^S	B^T	$\bar{V}_L$	$\bar{V}_T$	B^S
Ih	1.40	3.97	1.96	99.6	99.6	3.96	1.88	102.5
II	2.83	4.31	2.28	138.9	145.9	--	--	--
III	2.76	3.70	1.98	98.7	96.7	3.67	2.07	89.0
V	4.80	4.20	2.20	141.9	139.3	4.21	2.23	138.4
VI	7.77	4.55	2.35	181.4	184.3	4.52	2.53	158.8

* Taken from [10].

TABLE III: SYNOPSIS OF RESULTS FROM THE DIFFERENT PHASES (CONT'D)

Phase	Pressure (kbar)	Density (g/cm³)	Shear Modulus (kbar)	Density* (g/cm³)	Shear Modulus* (kbar)
Ih	1.40	.937	36	.934	33
II	2.83	1.193	62	--	--
III	2.76	1.166	46	1.148	49
V	4.80	1.267	61	1.248	62
VI	7.77	1.360	75	1.336	85

* Taken from [10].

Acknowledgments

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COMMENTS

S.KIRBY

Your method of measuring the density of the various crystalline phases of H_2O requires the shear stresses at the ice-cell interface to relax in order for the length measurements to conform to the true volume change of the ice. If the ice phase is strong, then these shear stresses may not be relaxed. Do you observe such time-dependent relaxations and how can you be sure the density measurements are not contaminated by the strengths of the ice polymorphs ?

Answer :

Shear stresses were indeed initially present between the samples and the wall of the chamber. That is why the samples were given ample time (2 hours at the higher pressures) to dissipate such stresses through plastic flow. No change in sample volume occured after that. The relaxation time decreased rapidly with decreasing pressure. The agreement between the bulk moduli determined from the density measurements as compared to the moduli calculated from the velocity data seems to indicate that residual shear stresses were minimal, if not negligible.

W.F. KUHS

You have found some evidence that the bond-strengths in the ordered ices are higher than in the disordered ones. Is this not only accidentally so ? Can one define the differences in bond strength in terms of differences e.g. in the bond bending for the different ices, which has nothing to do with being disordered or not ?

Answer :

There is evidence that linear bonds are stronger than bent ones within either ordered or desordered phases. There is also evidence that ordered ices have stronger bonds than disordered ices if the range of bond angles are comparable. Furthermore, as mentioned in the paper, ordering seems to have a more dramatic effect in ices that have linear bonds than in those with nonlinear ones.

J. KLINGER

The correlation between heat conduction data and sound velocity should be easy to establish only in the temperature range where phonon scattering is controled by intrinsic processes. My question is now in what temperature range the heat conduction measurements have been done ?

Answer :

The thermal conductivities referred to correspond to a temperature of $\sim$ 250 K. Some of the values, of course, have been extrapolated to this temperature.