ELASTIC CONSTANTS OF ICE Ih, UP TO 2.8 KBAR, 
BY BRILLOUIN SPECTROSCOPY 
R. Gagnon, H. Kiefte, M. Clouter, E. Whalley

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Abstract

The technique of high resolution Brillouin spectroscopy has been used to determine accurately the hydrostatic pressure dependence of the elastic constants of ice Ih in the full pressure range of phase stability 0 - 2.8 kbar. The percentage changes in the adiabatic elastic constants $c_{11}$, $c_{12}$, $c_{13}$, $c_{33}$, $c_{44}$ and bulk modulus, over the pressure range, are 3.0, 7.2, 8.4, 2.8, -1.5 and 5.6 percent per kbar respectively. Longitudinal and transverse velocities for polycrystalline ice aggregates are also determined over the pressure range.

Experimental Technique and Analysis

Brillouin spectroscopy is a relatively new experimental technique whose development has paralleled that of the laser. Brillouin scattering of light is attributed to those inhomogeneities, or fluctuations, in the optical dielectric constant of the scattering medium that are associated with the propagation of
spontaneous thermally induced acoustic (elastic) waves. Theory [9] can successfully predict the intensity, polarization and frequency shift of the scattered light with the result that (for a single crystal) the spectrum consists of three sets of doublets located symmetrically about the incident (laser) frequency, one \( (L) \) associated predominantly with longitudinal acoustic waves and two \( (T_1 \) and \( T_2 \)) predominantly with transverse waves. The acoustic velocities are related directly to the frequency shifts via the usual Brillouin equation \[3,9\]. These shifts depend on crystal orientation and can be precisely measured by Fabry-Perot interferometry. Brillouin spectra are therefore recorded at a series of different ice crystal orientations and yield an accurate determination of the elastic constants [10].

The Brillouin spectrometer used in these experiments has been described in other publications \[2,10\]. The incident light was provided by the 514.5 nm line of a single-mode argon-ion laser. The scattered light was spatially filtered and analyzed at 90° with a piezoelectrically scanned triple pass Fabry-Perot interferometer (of free spectral range 24.98 GHz) and detected by a cooled photomultiplier tube. The output from the photomultiplier was coupled to a data acquisition and stabilization system (Burleigh DAS-1). The multichannel analyzer of the DAS system accumulated spectral data in the form of photon counts (intensity) versus channel number (proportional to the frequency shift of the scattered light).

The ice samples were held in a high pressure cell which was constructed at the National Research Council of Canada and is shown in detail in Figure 1. Essentially it consists of a solid rectangular block of heat treated 300 maraging steel with two orthogonal intersecting channels such that there are a lower opening and two side openings allowing for the insertion of thick glass optical windows, contact mounted to polished steel ports, and a top opening allowing for a rotation stem assembly securely holding the sample. In addition, O-rings, backed by beryllium copper rings, were used for pressure-sealing the inner chamber. The hydraulic medium used was a clear oil (dioctyl sebacate), commonly known as Monoplex. Pressurization was done by means of a 3 kbar hand pump.

The cell was kept at a temperature of -35.5°C in order not to melt the sample on pressurization. The pressure was measured with a 3 kbar Heise gage. Cooling was accomplished by enclosing the cell in an evacuated plexiglass cryostat, and using four thermoelectric modules with "cold faces" attached to the sides of the cell (see Figure 1). Heat from the "hot faces" of the thermal modules was dissipated using an antifreeze mixture circulated by a Neslab cooler. The temperature of the cell, and sample, was monitored and determined...
Ice Ih samples were obtained from a large piece of monocrystalline Mendenhall glacial ice [2,3]. A Melt extrusion technique was used to produce a very smooth cylindrical sample, ~19 mm long and ~4 mm diameter, so that its c-axis was oriented at about 45 degrees to the symmetry axis. To avoid error in knowledge of the experimental scattering angle great care was taken to make sure that the bottom of the cylindrical sample (through which the laser beam enters the specimen) was very flat, smooth and normal to the symmetry axis.

For each specimen it was necessary to determine the exact crystallographic c-axis orientation so that the angle between the crystal c-axis and the wave vector of the acoustic waves, $\gamma$, for each rotation setting in the high pressure cell, could be used in the analysis of the Brillouin frequency shift data. To this end, an apparatus was constructed which made use of the birefringence of ice Ih. Frequency shift data were obtained at -35.5°C from two independent samples of Mendenhall glacial ice. The experiments were performed by orienting the sample to a particular $\gamma$ angle and then running a series of seven experiments, one at each of the pressures 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 2.8 kbar. About 16 Brillouin spectra, roughly evenly distributed throughout the whole range of $\gamma$ angles (i.e. 0° - 90°), were obtained from the two crystals at each pressure. The spectra were generally obtained during runs of a few hours, depending on the intensity of the transverse signals (see ref. 3). The elastic constants (Table I) for each pressure were determined by minimizing, via a modified Newton-Raphson iterative technique, the squared error generated from the differences between measured and calculated frequency shifts using the standard closed-form equations [10]. Each pressure involved about 36 measured shifts.

Table I. Parameters Determined for Ice Ih at -35.5°C

<table>
<thead>
<tr>
<th>Pressure (kbar)</th>
<th>Density (g/cm³)</th>
<th>Refractive Index</th>
<th>Elastic Constants (kbar)</th>
<th>Bulk Modulus</th>
<th>Average Velocity (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho$</td>
<td>$n$</td>
<td>$C_{11}$</td>
<td>$C_{12}$</td>
<td>$C_{13}$</td>
</tr>
<tr>
<td>0.00</td>
<td>.9228</td>
<td>1.3141</td>
<td>144.8</td>
<td>73.5</td>
<td>59.7</td>
</tr>
<tr>
<td>0.50</td>
<td>.9279</td>
<td>1.3160</td>
<td>147.3</td>
<td>76.3</td>
<td>61.9</td>
</tr>
<tr>
<td>1.01</td>
<td>.9329</td>
<td>1.3179</td>
<td>149.7</td>
<td>78.6</td>
<td>65.1</td>
</tr>
<tr>
<td>1.51</td>
<td>.9378</td>
<td>1.3197</td>
<td>151.8</td>
<td>82.3</td>
<td>67.7</td>
</tr>
<tr>
<td>2.01</td>
<td>.9426</td>
<td>1.3215</td>
<td>153.4</td>
<td>83.3</td>
<td>70.8</td>
</tr>
<tr>
<td>2.50</td>
<td>.9473</td>
<td>1.3232</td>
<td>155.8</td>
<td>86.7</td>
<td>71.7</td>
</tr>
<tr>
<td>2.80</td>
<td>.9500</td>
<td>1.3242</td>
<td>157.1</td>
<td>88.8</td>
<td>73.1</td>
</tr>
</tbody>
</table>

*Parameters calculated (from above) at -3°C for comparison to Gammon et al. [1] (see text).

It was also necessary to specify the density, $\rho$, and the refractive index, $n$, of the ice samples. The Lorentz-Lorenz relation, calibrated using Gammon's [3] refractive index and density of ice at -16°C and zero pressure, was used to determine the refractive indices from the densities at the different pressures and temperatures. The zero pressure density at -35.5°C was calculated from the expression for the temperature dependence of the density given by Gammon. The pressure dependence of the density of ice Ih was also required. To obtain this, the zero pressure adiabatic elastic constants (as measured in the present work) were first converted to isothermal values, in order to obtain the isothermal bulk modulus $B^T$ [11,12]. See Gammon [3] for a complete discussion, and parameters used. The assumed form of the isothermal bulk modulus was $B^T(P)=B_0^T+\Delta B/P$, where $P$ is pressure, $B_0^T$ is the bulk modulus at zero pressure and an estimate of $\Delta B/P$ was made using the data of Polian and Grimsditch [4]. This expression was then used to obtain the ice density by integrating the reciprocal of the bulk modulus. The preliminary densities and refractive indices of ice at the 6 elevated pressures were determined in this manner. These parameters were then used, along with the frequency shift data, to compute the elastic constants at each pressure. These elastic constants were,
in turn, used to obtain a better expression for the bulk modulus so that more accurate densities and refractive indices could be calculated and improved elastic constants could be computed. This procedure was iterated a couple of times, resulting in a completely self-consistent set of densities, refractive indices and elastic constants for ice Ih at 7 different pressures spanning the region of phase stability at \(-35.5^\circ C\).

Results and Discussion

Table I summarizes the results from the entire set of experiments. The elastic constants included in the table are adiabatic values. The five elastic constants were least-squares (quadratically) fitted to the pressure so that values could be obtained at any pressure within the region of phase stability. Similar expressions are derived for density and adiabatic (\(B^S\)) and isothermal (\(B^T\)) bulk moduli as given below:

\[
\begin{align*}
c_{11}(P) &= 144.951 + 4.6648 \times 10^{-1} P - 1.3501 \times 10^{-1} P^2 \\
c_{12}(P) &= 73.617 + 5.0743 P + 8.5917 \times 10^{-2} P^2 \\
c_{13}(P) &= 59.289 + 6.4189 P - 5.2490 \times 10^{-1} P^2 \\
c_{33}(P) &= 156.415 + 4.7546 P - 1.1307 \times 10^{-1} P^2 \\
c_{44}(P) &= 31.510 - 0.5662 P + 3.6917 \times 10^{-2} P^2 \\
\rho(P) &= 92.296 + 1.0247 \times 10^{-1} P - 1.8869 \times 10^{-4} P^2 \\
B^S(P) &= 92.296 + 5.5533 P - 0.26104 P^2 \\
B^T(P) &= 89.684 + 5.3668 P - 0.25215 P^2
\end{align*}
\]

\(P\) is pressure in kbars, the \(c_{ij}\)'s are the elastic constants in kbars and \(\rho\) is the density in g/cm\(^3\).

In Figure 2 are shown the "best" fit curves of acoustic velocity versus angle \(\gamma\) for various pressures. Experimental points on the average fall well within 0.1\% of the best fit values (see, for example, Figure 3 in ref. 2). As discussed in detail [3] the estimated absolute (systematic) uncertainty in the elastic constants is \(\pm 1\%\) and is primarily due to possible uncertainty in the scattering angle or experimental geometry.

The temperature dependence of the elastic constants was obtained by first accurately measuring the variations in longitudinal Brillouin frequency shift, at one sample orientation at \(0.5\) kbar, which resulted when the temperature was varied from \(-35^\circ C\) to \(-4^\circ C\) in \(-4^\circ C\) increments. This same temperature dependence was then assumed to pertain to all orientations of the sample, and was applied to the frequency shifts obtained at zero pressure and \(-35.5^\circ C\). Elastic constants were then computed from the temperature adjusted data, and quadratically fitted to the temperature to yield the following expressions:

\[
\begin{align*}
c_{11}(T) &= 136.813 - 28.941 \times 10^{-2} T - 17.827 \times 10^{-4} T^2 \\
c_{12}(T) &= 69.420 - 14.673 \times 10^{-2} T - 90.362 \times 10^{-5} T^2 \\
c_{13}(T) &= 56.341 - 11.916 \times 10^{-2} T - 73.120 \times 10^{-5} T^2 \\
c_{33}(T) &= 147.607 - 31.129 \times 10^{-2} T - 18.948 \times 10^{-4} T^2 \\
c_{44}(T) &= 29.726 - 62.874 \times 10^{-3} T - 38.956 \times 10^{-5} T^2
\end{align*}
\]

where \(T\) is in \(^\circ C\) and \(c_{ij}\)'s are in kbars.

These temperature dependence expressions were used to calculate the elastic constant data at \(-3^\circ C\) from the present data (see Table I). Agreement well within 1\% (on average 0.7\%) is noted with artificial ice results of Gammon [1] using a similar well-defined cylindrical sample geometry. The temperature corrections (2) above give results close to those obtained by Dantl's temperature dependence expression [6].

In Figure 3 are shown, the percentage variations in the elastic constants versus pressure. Immediately obvious is the negative pressure dependence of \(c_{44}\). This can be interpreted as an indication of softening of the shear modes and decreasing crystal stability before the phase transforms to another structure.
Figure 2. Velocities, for L, T₁, and T₂ acoustic modes, versus angle γ calculated from the "best" fit elastic constants at pressure 0, 1.0, 2.0 and 2.8 kbar for Mendenhall ice at -35.5°C.

Figure 3. Percentage change in elastic constants c₁₁, c₁₂, c₁₃, c₃₃ and c₄₄ versus pressure for Mendenhall ice at -35.5°C.

These results can be compared to the only other elastic constant pressure dependence work of Brockamp and Rütter [7]. These ultrasonic pulse transmission experiments were conducted on single crystals of ice to a maximum pressure of 0.4 kbars, at -20.5°C. Values from the present study for the percentage changes in the elastic constants were calculated from expressions (2) for the elastic constants at a pressure of 1.4 kbars (i.e. at mid-range). The values obtained were 2.96, 7.22, 8.35, 2.84 and -1.47 percent per kbar for ij = 11, 12, 13, 33 and 44 respectively. This can be compared to the ultrasonic values 2.98, 8.85, 7.63, 2.48 and -1.26 respectively [7]. The present results, however, are considered to be much more accurate because a full range of γ angles were used.

The elastic properties of polycrystalline aggregates must take into account the various sizes, shapes, and orientations of the crystallites that comprise the medium. However, if the grain orientations are assumed to follow a uniform random distribution, and a sample includes a large number of such grains, then the bulk elastic properties should be very nearly isotropic. In the present work a good estimate for the velocity of longitudinal acoustic waves in aggregates was obtained by suitably averaging the velocities over the complete range of propagation direction available within a crystal, as discussed in ref. [3]. The results for each pressure are shown in Table I. Experimental verification was carried out by conducting Brillouin scattering experiments on actual polycrystalline aggregates, at zero pressure, produced using the method described in the following paper. The mean longitudinal velocity, Vₐ, 3.926 km/s determined from 4 experiments on three such independent samples, was in excellent agreement with the calculated value (3.914 km/s). These results were also in excellent agreement (within .5%) with the value determined by Shaw [8] using ultrasonics on polycrystalline samples. The velocity of transverse acoustic waves in aggregates were calculated from Vₐ, ρ and B², and are shown in Table I. The variations of the mean longitudinal and transverse velocity versus pressure
are shown in Figure 4. Note in particular that \( V_T \) decreases with pressure indicating clearly, as pointed out above, decreasing crystal stability.

The present work represents an accurate and complete analysis of the elastic properties of ice Ih as a function of hydrostatic pressure and should prove useful for gaining a better understanding of ice, and the important role of hydrogen bonding, and also for engineering applications involving ice management. The bulk elastic properties for given natural samples are (of course) dependent on differing grain texture and presence, and extent, of various kinds of inclusions [2,3].

![Figure 4. Percentage change in the calculated "mean" longitudinal and transverse acoustic velocities, as expected in polycrystalline aggregates, versus pressure for Mendenhall ice at -35.5°C.](image)

Acknowledgments

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References