Ab initio simulation of the ice II structure

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We have carried out ab initio simulations on the high-pressure polymorph of solid water, ice II, a phase for which there is a surprising lack of experimental data. We report our calculated third-order Birch–Murnaghan equation of state for ice II: the zero pressure and temperature density, $\rho_0 = 1.240.27\pm0.62\,\text{kg}\,\text{m}^{-3}$, bulk modulus, $K_0 = 16.18\pm0.12\,\text{GPa}$, with the first pressure derivative of the bulk modulus, $K'_0$, fixed equal to 6.0. These parameters, the unit cell dimensions, and the atomic positions are in good agreement with experimental values. We also describe the way in which the change in unit cell volume is accommodated within the structure, primarily by contraction of the distance between neighboring hexagonal tubes—the principal structural element of ice II. This is in agreement with existing experimental data. © 2003 American Institute of Physics. [DOI: 10.1063/1.1593630]

I. INTRODUCTION

Ice II is a crystalline polymorph of solid water which is formed under moderate pressure (Fig. 1). Compression of ordinary hexagonal ice I leads to the formation of ice II at $\sim0.2\,\text{GPa}$. Compression beyond $\sim0.5\,\text{GPa}$ transforms ice II into denser polymorphs, ice V or ice VI. Ice II does not melt to liquid water; heating above $\sim240\,\text{K}$ causes a phase change to either ice III, V, or VI depending on pressure. Ice III may persist metastably upon cooling into the stability field of ice II, but ice II cannot be superheated above the II–III transition line. Ice II is unique among the low-pressure polymorphs (i.e., $<2\,\text{GPa}$) in that it has an ordered proton arrangement throughout its stability field. Ice II is also of interest because its structure (described in Sec. II) permits the inclusion of small atoms, such as hydrogen, helium, and neon, to form so-called “stuffed” ices. These have very different phase boundaries and physical properties to pure ice II, and their occurrence is known to complicate experiments in which the pressure transmitting medium can permeate the structure.

In addition to its intrinsic value to materials science, ice II is very likely to be an important planetary mineral. Pressure and temperature conditions within a large proportion of the Solar System’s icy moons are suitable for the stability of ice II: inside a large icy moon, such as the Jovian satellite Ganymede, ice II may form a layer several hundred kilometers deep. The physical properties of ice II are therefore pertinent to an understanding of the geophysics of icy moons influencing, amongst other things, the convective regimes in their interiors.

It is thus surprising that we know so little about ice II. Structural analyses, via x-ray and neutron diffraction, have been carried out at ambient pressures (upon quenched samples) and within the stability field of ice II. Of the latter, only Lobban et al. can categorically assert that their structure was “pure” ice II, and even their structure refinements were affected by the formation of cage-clathrates with the argon pressure medium. Indeed, this very recent work of Lobban et al. provides us with the only three reliable structural data points within the stability field of ice II.

The density of ice II was measured from 0.23 to 0.33 GPa at 237.65 K in a piston apparatus by Gagnon et al. in addition, Brillouin spectroscopy was used to determine the bulk modulus. Lobban et al. estimated the bulk modulus from just two data points at 200 K and found a similar value to Gagnon et al.

Piston compression experiments on both H$_2$O and D$_2$O ice have been carried out to explore phase boundaries between high-pressure polymorphs. However, the phase boundaries observed by these workers disagree with the equilibrium phase boundaries observed in other experiments, and since there was no independent identification of phases (e.g., by x-ray diffraction), it is at least possible that their proposed ice Ih-II boundary actually represents the transformation of ice Ih to an amorphous solid, as seen for example by Mishima et al. or ice IX.

Previous computational studies of ice II have concentrated on calculating the vibrational densities of states for comparison with inelastic incoherent neutron scattering spectra. Baez and Clancy used a point charge model to calculate the density of ice II at atmospheric pressure from 180 to 320 K.

Computational simulation of ice II has a number of benefits. We can calculate the properties of wholly uncontaminated ice II. This allows for the improved definition of structural changes which occur when other substances are occluded within the crystal. Density functional theory (DFT) calculations allow us to determine the density and elasticity of ice II at absolute zero temperature, typically to better than 2%. This helps constrain as yet unmeasured properties such as the thermal expansivity and the temperature dependence of the bulk modulus. Furthermore, we can study ice II at pressures far outside its stability field. In this study

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we have made calculations over a pressure range approximately ten times larger than the natural stability field of ice II. Access to this wider phase space permits the characterization of very small structural changes, such as the pressure strengthening of hydrogen bonds or changes in the shape of the unit cell, which may be too small to be observed experimentally.

We will commence with a description of the ice II structure (Sec. II), followed by our computation method (Sec. III); our results are presented in Sec. IV.

### II. STRUCTURE OF ICE II

The crystal structure of ice II is trigonal, space-group $R\bar{3}$, with primitive unit cell dimensions, $a = 7.78$ Å and $a = 113.1°$ at atmospheric pressure and 123.15 K. The fractional coordinates of atoms in the asymmetric unit are quoted in Table I. The crystal is composed of two varieties of hexagonal rings (hereafter 6A- and 6B-rings) of hydrogen bonded water molecules. For the purposes of describing the arrangement of these rings it is convenient to adopt the non-primitive hexagonal setting of space-group $R\bar{3}$: the two types of 6-rings are stacked alternately parallel to the $c$ axis, forming six-sided columns (6-tubes), as shown in Figs. 2(a) and 2(b). The dangling O–H bonds of the 6A-rings extend outwards, although not quite perpendicular to the $c$ axis, forming hydrogen bonds from 6A-rings in one column to 6B-rings in another (Fig. 3). The dangling O–H bonds of the 6B-rings are directed alternately up and down the $c$ axis, although not precisely parallel to it, binding adjacent 6A- and 6B-rings into tubes. This arrangement leads to the 6A-rings being relatively flat, and the 6B-rings being more corrugated, or puckered. Adjacent rings along the 6-tubes are rotated by $\sim 16°$ relative to one another. The structure preserves the open tetrahedral bonding of low-pressure ice Ih yet yields a higher density crystal.

Figure 3 also serves to introduce our notation for describing the different interatomic distances, as will be used in Sec. IV B. Interatomic distances within the flat and puckered 6-rings are denoted with the subscripts 6A and 6B; for example, $r(O–H)_{6A}$ or $r(O...O)_{6B}$. The diagonal diameters of the 6-rings, the distance between oxygen atoms on opposing corners, are $d_{6A}$ and $d_{6B}$ respectively. Interatomic distances between adjacent rings in the same 6-tube are $r(O–H)_1$, $r(H...O)_1$, $r(O...O)_1$, whereas those between rings in neighboring 6-tubes are $r(O–H)_{1}$, $r(H...O)_{1}$, and $r(O...O)_{1}$.

### III. COMPUTATIONAL METHODS

The plane-wave pseudopotential method, based on density functional theory, was used for calculating the total energy of the crystal lattice. The Perdew–Wang generalized gradient corrected functional (PW91) was applied to repre-

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**TABLE I. Comparison of calculation results at 0.474 GPa and 0 K with neutron diffraction data acquired at 0.48 GPa and 200 K.**

<table>
<thead>
<tr>
<th></th>
<th>Ice II experiment$^a$</th>
<th>Ice II simulation$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>7.7081(1)</td>
<td>7.551</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>113.119(1)$^c$</td>
<td>112.914$^c$</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>295.54(1)</td>
<td>281.385</td>
</tr>
<tr>
<td>$\rho$ (kg m$^{-3}$)$^c$</td>
<td>1214.69(4)</td>
<td>1275.79</td>
</tr>
</tbody>
</table>

$^a$Reference 8: At 0.48 GPa and 200 K. The authors published their results in the hexagonal setting of space-group $R\bar{3}$, but we have converted the cell dimensions and fractional atomic coordinates to the trigonal setting for ease of comparison.

$^b$This work: At 0.474 GPa and 0 K.

$^c$For hydrogenous ice II; note that in Ref. 8, the density is quoted for deuterated ice II.
sent the exchange-correlation potential,\textsuperscript{19} this form of the
generalized gradient approximation (GGA) having been
demonstrated to yield the most accurate results in hydrogen-
bonded systems\textsuperscript{20} despite not correctly representing disper-
sion forces. We have previously employed this GGA func-
tional with success for ices VIII and X,\textsuperscript{21} solid ammonia,\textsuperscript{21}
ammonia monohydrate,\textsuperscript{22} and ammonia dihydrate.\textsuperscript{23} Core
electrons are replaced by Vanderbilt non-norm-conserving ultrasoft pseudopotentials,\textsuperscript{24} themselves formulated within
the GGA, and the valence electron wave functions are ex-

danced as a plane-wave basis set. Total energy calculations
were performed using the VASP (Vienna \textit{Ab Initio} Simulation Package) code.\textsuperscript{25} Convergence tests were carried out to
optimize the sampling of the Brillouin zone, and the cut-off
of the plane-wave basis set: The Monkhorst–Pack scheme\textsuperscript{26}
was used for sampling of the Brillouin zone. It was found
that a $4 \times 4 \times 4$ grid with 32 symmetrically unique $\bar{k}$-points
in the irreducible wedge, combined with a kinetic energy
cut-off of 900 eV, yielded total energy convergence to better
than $10^{-4}$ eV per primitive unit cell. A series of fixed vol-

tume calculations were then performed in which the ions
were allowed to move according to the calculated Hellman–
Feynman forces. For each volume specified the structure was
relaxed via the conjugate-gradient technique in order to op-
timize the lattice parameters and internal coordinates.

In the following section we report the results of struc-
tural relaxations for ice II, which were started from the am-
bient pressure experimental structure of Kamb\textsuperscript{3} using the
trigonal primitive unit cell setting of space group $R\bar{3}$.

\section*{IV. RESULTS}

\subsection*{A. Equation of state}

Structural relaxations were carried out at a series of fixed primitive unit cell volumes from $\sim 250$ to $\sim 300$ Å$^3$ (cover-
ing the pressure range from $-1$ to 3.5 GPa) at which the
total energy of the crystal was calculated. A third-order
Birch–Murnaghan equation of state (EOS)\textsuperscript{27} was fitted to the
$E(V)$ and $P(V)$ data to determine the zero-pressure density, $\rho_0$, the zero-pressure bulk modulus, $K_0$, and its first pres-
sure derivative, $(\partial K/\partial P)_0$ or $K'_0$. Nonlinear regression
yielded an initial value for $K'_0$ of $6.17 \pm 0.28$ (with $V_0$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{(a) A representation of the ice II structure viewed down the $c$ axis of
the nonprimitive hexagonal cell. Observe that the structure consists of a
"sheaf" of 6-tubes (shaded gray) parallel to the $c$ axis. (b) A representation
of the ice II structure viewed perpendicular to the $c$ axis of the nonprimitive
hexagonal cell, showing the lateral bonding of 6A- and 6B-rings to join the
6-tubes (shaded gray) together.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Detail showing the arrange-
mint of the water molecules in the
6A- and 6B-rings, and the disposition
of the hydrogen bonds (dashed lines)
which join them together.}
\end{figure}
\[ V_0 = 289.44 \pm 0.15 \text{ Å}^3 \text{ and } K_0 = 16.06 \pm 0.25 \text{ GPa} \]. Cruz León et al.\textsuperscript{28} used the experimental compression data of Bizhigitov\textsuperscript{29} to derive a value of 6.0 for \( K_0 \), and so we opted to repeat the EOS fit with \( K_0' \) fixed identical to 6.0. This yielded improved standard errors for the remaining two variables, and our result for the EOS of ice II in the athermal limit is, \( \rho_0 = 1240.27 \pm 0.62 \text{ kg m}^{-3} \) (\( V_0 = 289.44 \pm 0.15 \text{ Å}^3 \), \( K_0 = 16.18 \pm 0.12 \text{ GPa} \), and \( K_0' = 6.0 \)).

The bulk modulus of ice II has been determined from acoustic measurements to be 14.39 GPa at 0.283 GPa and 237.65 K.\textsuperscript{9} Thus, assuming \( \rho_0 \) to be 1169 kg m\(^{-3} \). For our calculated value of \( K_0 \) to be accurate we therefore require the crystal to stiffen by a little over 3 GPa as the structure is cooled from \( \sim 240 \text{ K} \) to absolute zero. This is a perfectly reasonable value—the bulk modulus of ice Ih increases by \( \sim 2 \text{ GPa} \) from 0 to 240 K\textsuperscript{30,31}—although it remains for the low temperature bulk modulus of ice II to be measured experimentally.

Similarly, the thermal expansivity of ice II has not yet been directly measured. The best value currently available is an estimate derived from just two data points at 0.42 GPa.\textsuperscript{8} The ambient pressure densities\textsuperscript{3–5} are grossly inconsistent with one another, so it is not possible for us to confidently assess the accuracy of our calculated value of \( \rho_0 \) using them. The most reliable experimental points are those at 0.42 GPa,\textsuperscript{8} and a straight line drawn through these points extrapolates to a zero Kelvin density of 1268.97 kg m\(^{-3} \). Our calculated EOS yields a density at 0.42 GPa of 1270.58 kg m\(^{-3} \). Of course, one would not expect the density to vary perfectly linearly with temperature, but should instead tend toward \( d\rho/dT \rightarrow 0 \) as \( T \rightarrow 0 \text{ K} \). This suggests that our value of \( \rho_0 \) is slightly too large. However, our experience with other ice polymorphs,\textsuperscript{21} and with the water-rich ammonia hydrates,\textsuperscript{22,23} leads us to expect that \( \rho_0 \) is not in error by more than \( \sim 2 \% \). Indeed, bearing in mind that reducing \( \rho_0 \) also softens \( K_0 \), an error in \( \rho_0 \) greater than 4\% would yield \( dK/dT \rightarrow 0 \) from 0 to 240 K, which is most improbable. There is a very clear need to measure the thermal expansivity of ice II in detail.

**B. Structural changes under pressure**

We derived a range of internal parameters, as well as the unit cell dimensions, from each volume relaxation. These included each of the different types of covalent H–O bond, H...O hydrogen bond, and O...O separation. We also observed the change in the diameter of the two types of 6-rings, and the variation in the many H–O–H angles in the structure. Second-order polynomials were fitted to these results (Fig. 4 gives an example), and the parameters from all of these polynomial fits are quoted in Table II. We will briefly discuss our findings and relate them to the experimental data.

The unit cell of ice II undergoes only a very slight change in shape over the pressure range we examined. The rhombohedral angle, \( \alpha \), increased by approximately 0.2\(^{\circ} \), the pressure dependence being given by a second-order polynomial: \( \alpha = 112.85^{\circ} + 0.1062P - 0.0127P^2 \) (with \( P \) in GPa). Over the pressure range studied by Lobban et al.,\textsuperscript{8} our calculations show that one should expect \( \alpha \) to increase by 0.019\(^{\circ} \). In terms of the nonprimitive hexagonal \( c/\alpha \) ratio, this translates to a change in \( c/\alpha \) of \( \sim 0.00074 \). Lobban et al.\textsuperscript{8} report that \( c/\alpha \) changes by \(-0.00066(2) \) from 0.28 to 0.48 GPa at 200 K; this is in agreement with both the sign and the magnitude that our calculations indicate.

Table II shows that all of the covalent O–H bonds in our simulated cell increased in length very slightly with pressure. This occurs because the H...O hydrogen bonds increase in strength (and thus shorten) at a greater rate than the O...O separation decreases. This pressure strengthening of the hydrogen bond in ice is a well-known phenomenon that ultimately leads to the hydrogen-bond symmetrized form of ice called ice X. We have previously studied the increase in O–H bond lengths in ice VIII and found a pressure dependence in agreement with experimental data.\textsuperscript{21} Hence, the overall behavior of the interatomic bonds in ice II is not surprising. There are some interesting findings to be had in the detail however.

All of the bonds which form the 6A- and the 6B-rings exhibit near identical pressure dependencies. That the 6B-rings decrease in diameter more readily under pressure is due to changes in bond angles rather than bond lengths. It is noteworthy that the structure appears to compress dominantly as a result of the 6-tubes moving closer together: the rate at which the bonds joining the 6-tubes decrease in length is twice the rate at which the intra-ring bonds shrink, and it is \( \sim 50 \% \) greater than the rate at which bonds joining rings within the 6-tubes shrink. In effect, the 6-tubes are behaving like monocoques, wherein the bulk of the external load is carried through their walls. This is in agreement with the experimental observation of Lobban et al.,\textsuperscript{8} that increasing...
pressure drives the channels in the helium-free structure closer together.

Column four of Table II presents the experimental values for the tabulated bond length changes. In every single instance, the magnitude of the experimental standard error is larger than the calculated value of the change in bond length. The bond length changes are therefore so small that one cannot easily use the experimental data to arrive at useful conclusions as to how the structure behaves under compression; there must be a reduction in the standard errors of approximately an order of magnitude from those of Lobban et al. if we are to experimentally observe real structural changes in ice II under compression.

V. CONCLUSIONS

We have undertaken the first *ab initio* study of ice II across a range of pressures, presenting values for the athermal density and compressibility: \( \rho_0 = 1240.27 \pm 0.62 \, \text{kg} \, \text{m}^{-3} \), \( K_0 = 16.18 \pm 0.12 \, \text{GPa} \), and \( K_0' = 6.0 \). These values permit us to estimate the thermal expansivity and the temperature dependence of the bulk modulus. The lack of experimental data reveals the urgent need for a determination of the thermal expansivity of ice II.

We have also presented our calculations of the pressure dependencies of many internal bond lengths. These reveal that the structure compresses by shortening the distance between the main structural members, hexagonal tubes which themselves are relatively resistant to compression around their girth, but less so along their length, in agreement with observations from *in situ* neutron diffraction experiments. In all of the bonds examined, the change of bond length was found to be smaller than the errors in the best available experimental data.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Pressure dependence ( (P \text{ in GPa}) )</th>
<th>Change ( (\text{Å}) ) from 0.28 to 0.48 GPa(^a)</th>
<th>Change ( (\text{Å}) ) from 0.28 to 0.48 GPa(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r(O-H)_{6A} )</td>
<td>(-0.000 259P^2 + 0.002 987P + 1.003 063)</td>
<td>(0.000 558) (\pm 0.012)</td>
<td>(0.012 \pm 0.015)</td>
</tr>
<tr>
<td>( r(O-H)_{6B} )</td>
<td>(-0.000 319P^2 + 0.003 985P + 0.993 840)</td>
<td>(0.000 749) (\pm 0.020)</td>
<td>(0.020 \pm 0.013)</td>
</tr>
<tr>
<td>( r(O-H)_{7} )</td>
<td>(-0.000 254P^2 + 0.003 339P + 0.997 569)</td>
<td>(0.000 629) (\pm 0.023)</td>
<td>(0.023 \pm 0.015)</td>
</tr>
<tr>
<td>( r(H...O)_{6A} )</td>
<td>(0.003 328P - 0.039 771P + 1.691 501)</td>
<td>(-0.007 44) (\pm 0.009)</td>
<td>(-0.009 \pm 0.014)</td>
</tr>
<tr>
<td>( r(H...O)_{6B} )</td>
<td>(0.001 961P^2 - 0.038 545P + 1.720 096)</td>
<td>(-0.007 41) (\pm 0.003)</td>
<td>(-0.003 \pm 0.020)</td>
</tr>
<tr>
<td>( r(H...O)_{11} )</td>
<td>(0.010 440P^2 - 0.086 028P + 1.846 157)</td>
<td>(-0.015 62)</td>
<td>(-0.010 \pm 0.016)</td>
</tr>
<tr>
<td>( r(H...O)_{11} )</td>
<td>(0.005 642P^2 - 0.059 186P + 1.783 642)</td>
<td>(-0.010 98)</td>
<td>(-0.006 \pm 0.019)</td>
</tr>
<tr>
<td>( r(O...O)_{6A} )</td>
<td>(0.003 270P^2 - 0.037 654P + 2.690 09)</td>
<td>(-0.007 03)</td>
<td>(0.000 \pm 0.013)</td>
</tr>
<tr>
<td>( r(O...O)_{6B} )</td>
<td>(0.002 222P^2 - 0.037 935P + 2.708 256)</td>
<td>(-0.007 25)</td>
<td>(-0.031 \pm 0.017)</td>
</tr>
<tr>
<td>( r(O...O)_{11} )</td>
<td>(0.002 827P^2 - 0.080 824P + 2.831 469)</td>
<td>(-0.014 76)</td>
<td>(-0.034 \pm 0.017)</td>
</tr>
<tr>
<td>( r(O...O)_{11} )</td>
<td>(0.005 576P^2 - 0.056 197P + 2.763 110)</td>
<td>(-0.010 39)</td>
<td>(0.017 \pm 0.019)</td>
</tr>
<tr>
<td>( d_{6A} )</td>
<td>(0.005 137P^2 - 0.068 330P + 5.353 402)</td>
<td>(-0.012 89)</td>
<td>(0.004 \pm 0.015)</td>
</tr>
<tr>
<td>( d_{6B} )</td>
<td>(0.004 621P^2 - 0.075 252P + 5.212 510)</td>
<td>(-0.014 35)</td>
<td>(-0.046 \pm 0.017)</td>
</tr>
</tbody>
</table>

\(^a\)This work (athermal limit).
\(^b\)Reference 8 (200 K).

ACKNOWLEDGMENTS

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