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## Abstract

Neutron diffraction in combination with a gas pressure cell device allowed us to measure the lattice parameters of ordinary ice ($D_2O$ ice Ih) up to 5 kbar at 145 K under true hydrostatic pressure conditions. The results are compared with earlier studies and may reveal a more precise equation of state of ice Ih at 145 K. The elastic anisotropy was found to be very small in accordance with the very small anisotropy of thermal expansion. Nitrogen was used as the pressure medium, for which it is shown here that under the above experimental conditions no clathrate hydrates are formed.

## 1. Introduction

Despite the very rich phase diagram of water and ice under elevated pressure conditions, ordinary ice (ice Ih) exhibits two very specific features which are both intimately related to anharmonic effects in the lattice. First, below about 70 K ice Ih shows a negative thermal expansion (NTE) [1, 2] common to other tetrahedrally coordinated systems. Second, when compressed at low temperatures ($T < 130$ K) above ∼1.5 GPa,[6] ice Ih undergoes a transition to an amorphous phase (HDA) via a pressure-induced amorphization (PIA) [3]. We have recently shown [4] that these two striking properties of ice Ih are related to each other via a pronounced softening of transverse acoustic phonon branches with increasing pressure. In the course of this inelastic neutron scattering (INS) study on a single-crystal specimen of ice Ih we have developed experimental techniques which allowed us to carry out neutron diffraction experiments on ice under true hydrostatic pressure conditions without clathrate

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[6] 1 GPa = 10 kbar.

hydrate formation or solidification of the pressure medium. In what follows we summarize these experimental techniques and present precise values of the lattice parameters, the equation of state (EOS) and the elastic anisotropy of ice Ih at low temperatures up to pressures of 0.5 GPa under true hydrostatic conditions. To our knowledge and most likely due to mere experimental difficulties, these important properties of ice Ih have never been determined accurately before.

## 2. Experimental technique

Single crystals of ice Ih have been grown from the liquid phase by very slowly immersing a cuspid quartz ampoule filled with degassed $D_2O$ (99.90% deuterated/EURISO-TOP, Gif-sur-Yvette, France) into a bath of ethanol cooled to $-60\,°C$. Typically, growth of an ampoule of $\sim30$ cm$^3$ was completed within 5–7 days. Grown samples were then checked for defects and twins by visual observation under double-crossed polarized monochromatic light. Subsequently, pieces of 0.5–1.0 cm$^3$ were cut and preoriented at $T = -5\,°C$ by means of neutron diffraction in a specifically adapted mini-Dewar. All samples were of excellent quality with typical mosaic spread of less than $0.5°$. The preoriented samples were then loaded into the gas pressure cell which was mounted in a standard He cryostat suited for neutron diffraction. A two-stage compressor system allowed for gas pressures up to 0.55 GPa. Special care in the choice of the pressurizing gas must be taken as ice readily forms clathrate hydrates when exposed to gases at pressures more than typically 0.1 GPa, as e.g., in the case of He. Clathrate hydrates are formed when gas molecules (guests) penetrate the ice network (host), the latter forming cages around the guest molecules and thereby changing structure (see [5] and references therein). Depending on the size of the guest molecules, these clathrate hydrates are formed in two different types of structure up to a limiting guest molecule size where penetration into the host becomes ineffective. In order to avoid their formation, pressure transmitting gases with a relatively large molecule size are hence favoured. On the other hand these gases *per se* also exhibit relatively high solidification temperatures, which under the application of pressure further increase. Thus, a compromise must be found of a gas light enough not to freeze at low temperature when exposed to several kilobars of pressure, and nevertheless with molecules large enough not to penetrate the ice network, eventually forming clathrate hydrates. A further complication arises from the fact that experiments on ice Ih above 0.2 GPa pressure must be carried out at temperatures strictly below 155 K as otherwise ice Ih transforms into other ice phases (ices II and IX). It is hence of no practical use to carry out the measurements at $T > 145$ K to circumvent early solidification of the pressure medium with increasing pressure. On previous test runs we have found nitrogen to be the best choice in compromising both aspects, i.e. not forming clathrate hydrates up to 0.5 GPa (see below) and not freezing up to 0.55 GPa at 145 K [6][7].

In the course of the above-mentioned INS measurements on single-crystal samples of ice Ih, lattice parameters have been determined on the triple-axis spectrometer 1T1 at the Laboratoire Léon Brillouin (CEA Saclay, France). In order to enhance the resolution of the instrument an additional 10′ collimator has been inserted in the outgoing neutron beam, whereas for the INS measurements an all-open configuration of the instrument has been chosen.[8] Although greatly increasing the accuracy of the measured values of the lattice parameters, their determination from a very restricted set of Bragg peaks on a triple-axis instrument is known to be highly sensitive to systematic errors. Powder diffraction is generally a much better means to determine accurately lattice parameters. We have thus carried out additional measurements

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[7] The critical point of nitrogen is at 431 K/101 bar.
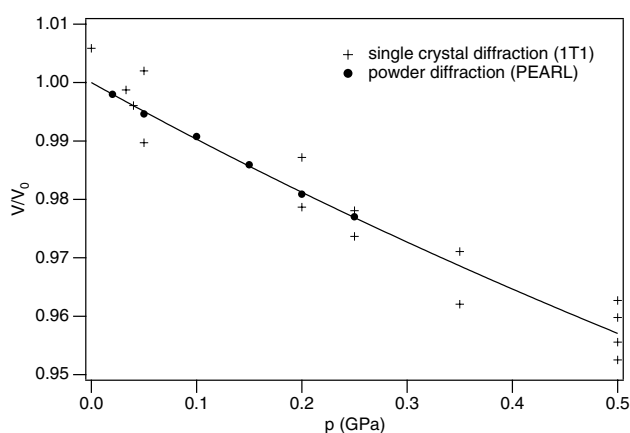[8] Incoming neutron wavelength $\lambda = 2.36$ Å.

**Figure 1.** Relative volume versus pressure from single-crystal (1T1) and powder (PEARL) neutron diffraction ($T = 145$ K). The line is a fit of the Murnaghan equation to the data.

on the TOF neutron powder diffractometer PEARL at ISIS (Rutherford Appleton Laboratory, UK). A similar gas pressure device mounted in a standard He cryostat was used. The sample was loaded into the zero-matrix cell in its liquid form and then cooled at 200 bar to freeze into ice Ih.[9] Likewise, nitrogen was used as the pressure medium. These measurements on PEARL were carried out not only to reveal more precise lattice parameters of ice Ih as a function of pressure but also to reconfirm our earlier conjecture, namely that no clathrate hydrates are formed from nitrogen at 145 K up to at least 0.5 GPa.

## 3. Results

On the triple-axis instrument 1T1 up to four Bragg reflections were measured before and after increasing the pressure. These were primarily measured in order to realign the sample for the subsequent INS measurements and thus yielded the lattice parameters just as additional measured variables. Hence, and due to the restricted reciprocal resolution of a thermal triple-axis instrument, the measured lattice parameters include fairly large errors. On the other hand, powder diffraction data obtained from PEARL were analysed within the GSAS Rietveld refinement package, resulting in much more precise values. Figure 1 compares the volume $V$ versus pressure $P$ relation of ice Ih, i.e. the equation of state (EOS), obtained from single-crystal and powder neutron diffraction. Obviously, values from the latter are of better quality, whereas the data from the triple-axis spectrometer show pronounced scattering. The $V(P)$ relation was fitted with the Murnaghan equation

$$V_0/V = \left( P\frac{B'}{B} + 1 \right)^{(1/B')} \tag{1}$$

with $V_0$, $B$ and $B'$ the volume at zero pressure, the bulk modulus and its first pressure derivative, respectively. The zero-pressure volume $V_0 = 128.18$ (129.9) Å$^3$ measured on PEARL (1T1) is in fair agreement with measured lattice parameters at ambient pressure and 145 K by x-ray diffraction ($V_0 = 128.588$ Å$^3$, [2]). The fitted isothermal values $B = 9.85(47)$ GPa and $B' = 6.6$ match well with adiabatic values found from Brillouin scattering measured at a higher temperature of $-35\,°C$ ($B = 9.23$ GPa) [7] and are in reasonable agreement with

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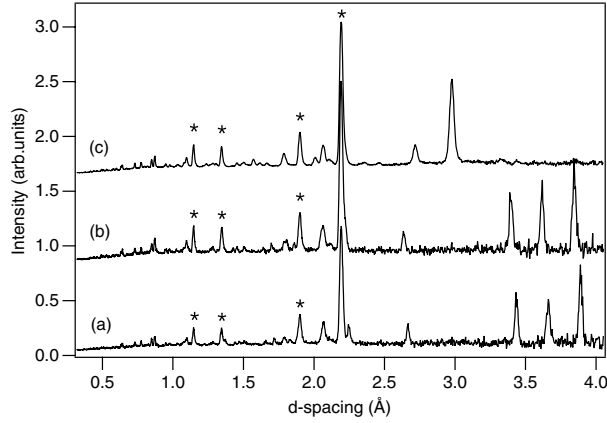[9] The zero-matrix alloy TiZr exhibits vanishing coherent elastic neutron scattering.

**Figure 2.** Neutron powder diffraction patterns measured on the TOF diffractometer PEARL: (a) sample at $T = 145$ K, $P = 0.02$ GPa; (b) sample isothermally compressed to $P = 0.5$ GPa ($T \equiv$ 145 K); (c) sample isobarically warmed up to $T = 161$ K ($P \equiv 0.5$ GPa). Stars indicate Bragg peaks from the cryostat. No additional peaks resulting from a clathrate phase can be identified.

**Table 1.** Lattice parameters, volume and $c/a$ ratio of $D_2O$ ice Ih at 145 K determined from neutron powder diffraction (PEARL).

| $P$ (GPa) | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $c/a$ |
|---|---|---|---|---|
| 0.02 | 4.492(1) | 7.319(2) | 127.91(7) | 1.6292(7) |
| 0.05 | 4.487(1) | 7.311(2) | 127.48(8) | 1.6293(8) |
| 0.10 | 4.482(1) | 7.301(2) | 126.99(7) | 1.6291(7) |
| 0.15 | 4.474(1) | 7.291(2) | 126.36(8) | 1.6297(7) |
| 0.20 | 4.466(1) | 7.277(2) | 125.72(7) | 1.6293(7) |
| 0.25 | 4.461(1) | 7.266(2) | 125.23(7) | 1.6287(7) |

ultrasonic measurements at 77 K ($B = 9.3$ GPa and $B' = 6$) [8]. Fixing $B' \equiv 6$ we find $B = 9.96(11)$ GPa.

Table 1 lists the lattice parameters, volume and $c/a$ ratio determined from the powder diffraction runs on PEARL up to 0.25 GPa. The $c/a$ ratio exhibits an almost vanishing pressure dependence in agreement with the nearly isotropic thermal expansion of ice Ih in the entire temperature range [1]. Very little pressure dependence in $c/a$ is indeed expected on the basis of the elastic constants $c_{ij}$ of ice Ih. Assuming pure hydrostatic conditions the relative change in the $c/a$ ratio calculates to

$$\frac{\delta(c/a)}{c/a} \sim \frac{c_{13} + c_{33} - (c_{11} + c_{12})}{(c_{11} + c_{12})c_{33} - 2c_{13}^2} P \tag{2}$$

where we assume $P \ll c_{11} + c_{12}$ and $P \ll c_{13}$. With values of the elastic constants at ambient pressure and $T = -20\,°C$ [9] we find $\delta(c/a)/(c/a) \sim -0.05\%$ between 0 and 0.5 GPa.

Finally, we show in figure 2(a) and (b) powder diffraction patterns of ice Ih at 0.02 and 0.5 GPa both measured at 145 K. Compared to the pattern at 0.02 GPa no additional peaks appear at 0.5 GPa. The formation of clathrate hydrate from nitrogen (nitrogen hydrate), at pressures as little as 0.02 GPa, can be ruled out. Furthermore, both patterns show no peaks at all in the range $2.8 < d < 3.3$ Å where the strongest reflections of nitrogen hydrate would be expected [5]. As evident from the phase diagram of ice, the sample transforms completely into ice IX when slowly warmed up at a constant pressure of 0.5 GPa (figure 2(c)). In addition to

these findings from powder diffraction, no deterioration of the excellent mosaic spread ($<0.5°$) of the single-crystal samples could be observed in the course of our INS measurements on 1T1 [4]. Hence we are confident that no clathrate formation occurred in our measurements.

## 4. Conclusions

The EOS of ordinary ice ($D_2O$ ice Ih) has been established under true hydrostatic conditions at 145 K up to 0.5 GPa. Major experimental difficulties originating from the formation of gas hydrates with the pressure medium can be circumvented by using nitrogen instead of helium in a gas pressure device. The observed very weak elastic anisotropy is in agreement with the almost isotropic thermal expansion and the elastic constants of ice Ih. The observed bulk modulus $B = 9.85$ GPa at $T = 145$ K is about 10% larger than published values at higher temperatures [7, 9]. Although an increase of $B$ with decreasing temperature is expected in any system exhibiting positive thermal expansion [10], the relative increase in the case of ice Ih seems to be especially pronounced. We point out, however, that a pronounced temperature dependence of the bulk modulus has been noted earlier for ice Ih [8] and for other ice phases [8, 11], and that, e.g., in the case of ice VIII the bulk modulus has been equally found to increase by about 15% from $T = 300$ K down to 100 K [11].

## Acknowledgments

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