

ISIS Experimental Report

Rutherford Appleton Laboratory

Title of Experiment: The thermal expansivity of ice II

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Introduction. The crystalline polymorph of solid water called ice II is the stable phase at pressures of ~ 0.2 GPa to ~ 0.5 GPa at temperatures below ~ 250 K. In common with many of the other known high-pressure phases, ice II is readily recoverable to atmospheric pressure after quenching to below ~ 120 K. Very little work has been done on ice II within its P-T stability field; in part this is due to problems encountered when helium is used as the pressure transmitting fluid. Helium penetrates the crystal structure of ice II to form a helium hydrate, the properties and phase relations of which differ significantly from pure ice II. To date therefore, there have been few studies of pure ice II under pressure.^{1,2} In order to study ice II at high pressure, argon must be used as the pressure transmitting medium. This poses a problem since the melting point of argon is so much higher than helium, effectively circumscribing that part of the ice II stability field which can be accessed. Our motivation for expanding on the earlier work by carrying out neutron diffraction experiments upon ice II was to measure the equation of state; the isothermal bulk modulus and the thermal expansivity. Ice II is likely to be a major rock-forming mineral in the outer Solar System;³ pressure and temperature conditions within a large proportion of the Solar System's icy moons are suitable for the stability of ice II. The physical properties of ice II are therefore pertinent to an understanding of the geophysics of icy moons.

Experimental method. Our experiments were carried out on HRPD using pressure cells composed of either Aluminium or TiZr null-scattering alloy. Liquid D₂O was loaded into the pressure vessels along with a small wad of silica wool to act as a nucleator. These were sealed under ~ 500 bar of argon gas, attached to a cryostat centre stick, and loaded into a vanadium-tailed helium cryostat. The cryostat was mounted in the neutron beam line, and the sample equilibrated at a temperature of 225 K, which resulted in the formation of polycrystalline ice Ih. Ice II was formed by pressurizing the sample, under argon gas, to ~ 2.5 kbar at 225 K, where the phase transformation takes place in a matter of minutes. Data were collected in the 90° detector banks; collection times adequate for refining the unit cell volume to better than one part in ten thousand were ~ 15 minutes in the Al cell, and ~ 25 minutes in the TiZr cell. Diffraction patterns were collected as a function of pressure within the stability field of ice II at temperatures *above* the melting line of argon. The sample was then decompressed and recovered to atmospheric pressure at 110 K after which diffraction patterns were collected in 5 K intervals from 5 – 175 K. Upon warming at ambient pressure, ice II (in common with other quenched high-pressure phases of ice) transforms to the cubic polytype of ice I. This was observed (in two sample loadings) to occur between 160 – 165 K. On one occasion, we warmed ice Ic to 225 K and compressed it to make a fresh sample of ice II; however, the cubic ice did not transform to ice II until a pressure of 0.35 GPa was applied, and yielded a strongly textured sample.

Results. In all of the experimental runs, difficulties were encountered with blockages of frozen argon in the pressure capillary running up through the middle of the cryostat centre stick, even when care was taken to warm the capillary. When this occurred we were unable to determine the pressure acting on the sample and the data had to be discarded. In three separate loadings (one in the Al cell and two in the TiZr cell), the following *usable* data sets were collected: In the stability field of ice II we collected data between 0.25 – 0.45 GPa, at 0.025 GPa intervals, along the 225 K isotherm. At ambient pressure,

we collected two sets of data in the Al cell, one from 5 – 80 K, and the second from 5 – 115 K. We collected one data set at a pressure of ~ 50 bar in the TiZr cell from 50 – 100 K, and one nominally at atmospheric pressure from 50 – 160 K. There were differences in the absolute unit cell volumes between these four data sets of about six parts in ten thousand, corresponding to a shift of the sample in the 100 metre flightpath of the neutron beam of ~ 2 mm. The ambient pressure data sets were therefore normalised such that the unit cell volumes were identical at 55 K (Fig. 1). Diffraction patterns were collected in the TiZr pressure cell at 9 pressure points from 0.25 – 0.45 GPa, at 0.025 GPa intervals, along the 225 K isotherm and refined to yield the unit cell volume (Fig. 2). These data were fitted with a third-order Birch-Murnaghan equation of state (BMEOS), the parameters of which are shown in Fig. 2.

Figure 1. Thermal expansion of ice II at room pressure.

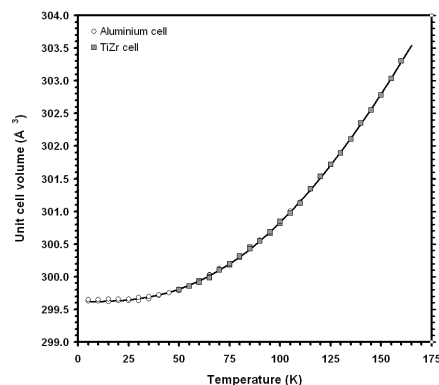
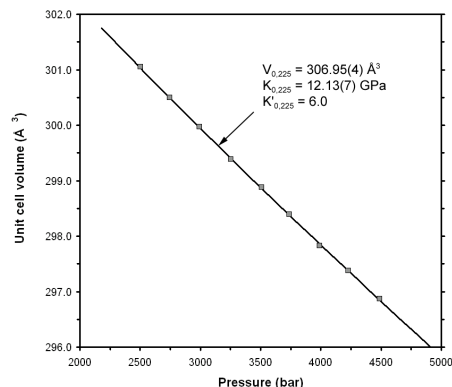


Figure 2. Isothermal compression of ice II at 225 K.



References

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