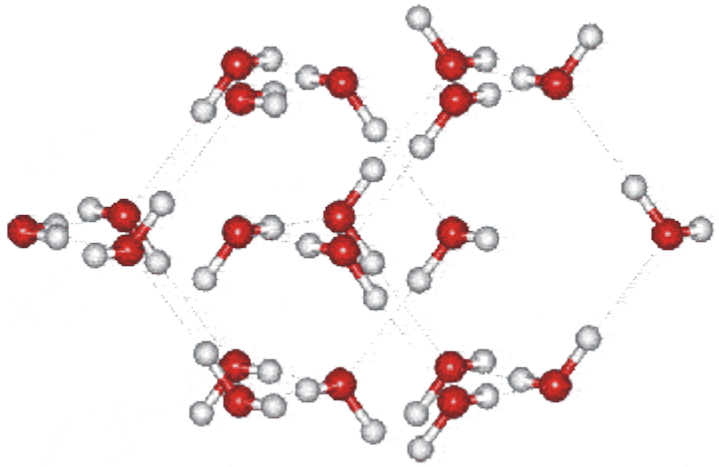
Ice-seven (Ice VII)

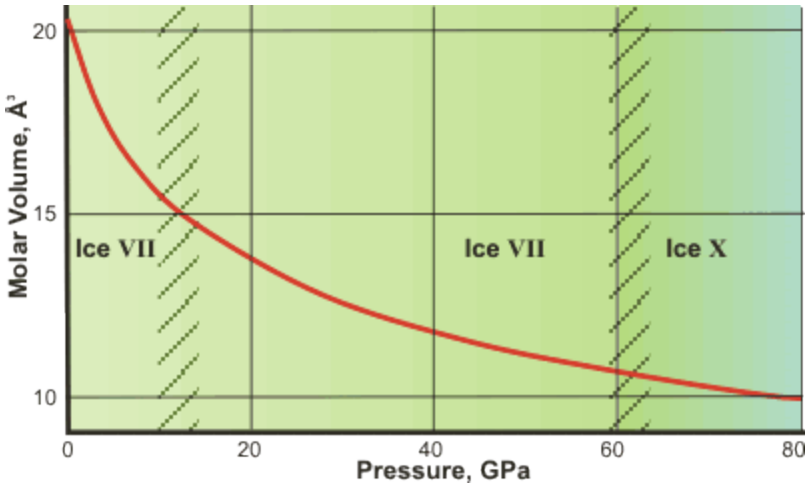
Ice-seven (ice VII) [1226] is formed from liquid water above 3 GPa by lowering its temperature to ambient temperatures (see Phase Diagram). It can be obtained at low temperature and ambient pressure by decompressing (D_2O) ice-six below 95 K and is metastable over a wide range of pressure, transforming into LDA above 120 K [948].



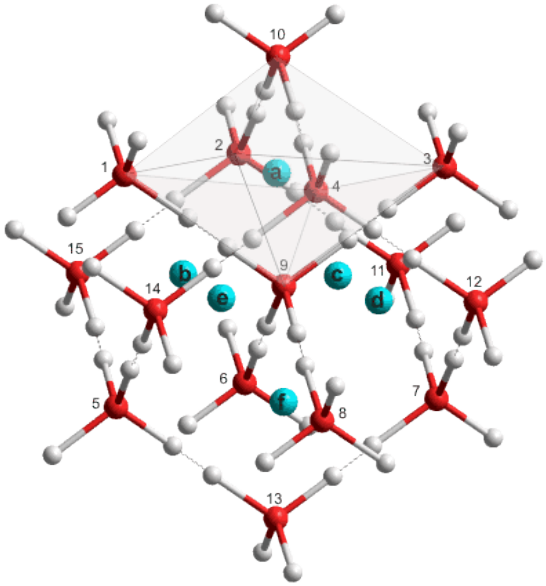
Note that in this structural diagram the hydrogen bonding is ordered whereas in reality it is random (obeying the 'ice rules': two hydrogen atoms near each oxygen, one hydrogen atom on each O···O bond). As the H-O-H angle does not vary much from that of the isolated molecule, the hydrogen bonds are not straight (although shown so in the figures).

The Ice VII unit cell, which forms cubic crystal ($Pn\bar{3}m$, 224; Laue class symmetry m-3m) consists of two interpenetrating cubic ice lattices with hydrogen bonds passing through the center of the water hexamers and no connecting hydrogen-bonds between lattices. It has a density of about 1.65 g cm^{-3} (at 2.5 GPa and 25 °C [8]), which is less than twice the cubic ice density as the intra-network O····O distances are 8% longer (at 0.1 MPa) to allow for the interpenetration. The cubic crystal (shown opposite) has cell dimensions 3.3501 Å (a, b, c, 90º, 90º, 90º; D_2O, at 2.6 GPa and 22 °C [361]) and contains two water molecules.

All molecules experience identical molecular environments. The hydrogen bonding is disordered and constantly changing as in hexagonal ice but ice-seven undergoes a proton disorder-order transition to ice-eight at about 5 °C; ice-seven and ice-eight having identical structures apart from the proton ordering. Ice-seven is metastable indefinitely at 77 K.



If the pressure is increased above about 14 GPa there are changes in the proton ordering [1428]. This is shown in the phase diagram and gives rise to a loss of the cubic symmetry. This is thought due to some dissociation with some hydrogen ions occupying the octahedral cavities, eventually rising at greater than 30 GPa to plateau at one interstitial occupancy to every two water molecules [2027]; this is equivalent to two of each six positions (as shown below right) being occupied. These interstial protons cannot form normal hydrogen bonds with the H2O oxygen atoms. At higher pressures, ice-seven undergo a continuous transition into cubic ice-ten (ice X) where most hydrogen atoms are situated midway between the oxygen atoms. The size of the ice crystal (two molar volumes per unit cell) continuously reduces over this large change in pressure with no obvious volume steps at the expected ice transitions [1943].



Shown opposite is a cartoon of ice-seven showing the octahedral interstitial cavities (shown as blue spheres a-f). The water molecules are shown with the positions of their four possible hydrogen atoms, although only two, or less, would be occupied obeying the 'ice rules'. Any interstitial hydrogen atoms (shown here labelled a-f) sit in the six octahedral cavities and are centered on the body-centered cubic square faces (as examples, octahedral cavity (a, shown gray) is made from the

water molecules 1, 2, 3, 4, 9 and 10 and sits in the square face made from the water molecules 1, 2, 3 and 4 of the body-centered cube centered on water molecule 9; cavity (e) is formed from the water molecules 1, 4, 5, 8, 9 and 14 and in the square face made from the water molecules 1, 4, 5 and 8 of the body-centered cube.; and cavity (f) is formed from the water molecules 5, 6, 7, 8, 9 and 13 and in the square face made from the water molecules 5, 6, 7 and 8 of the body-centered cube).

In contrast to ice Ih, high density ices may incorporate some solutes into their crystal structure. Ice-seven may incorporate up to ~7.5 wt % NaCl into the octahedral cavities (face centered positions of its body centered cubic structure, described above right) at high pressure (for example, 4-21 GPa) [955]. Counter-intuitively, this incorporation causes a reduction in the unit cell dimensions and a greater than expected increase in density [955].

Ice-seven has known triple points with ice-six and ice-eight (5 °C, 2.1 GPa), ice-eight and ice-ten (100 K, 62 GPa) and liquid water and ice-six (355 K, 2.216 GPa). Interestingly, at high pressures (~ 2.3 GPa), liquid water can be made to freeze at over 100 °C (to give the more dense ice-seven). The dielectric constant of ice-seven is about 150.

Interactive Jmol structures are given.

Source:http://www1.lsbu.ac.uk/water/ice_vii.html