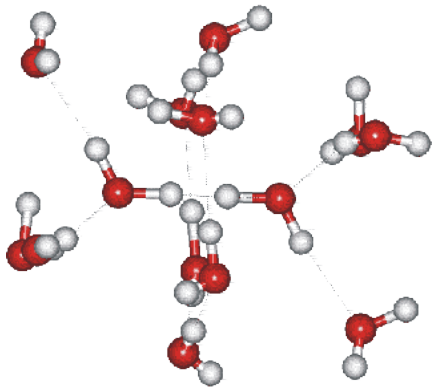
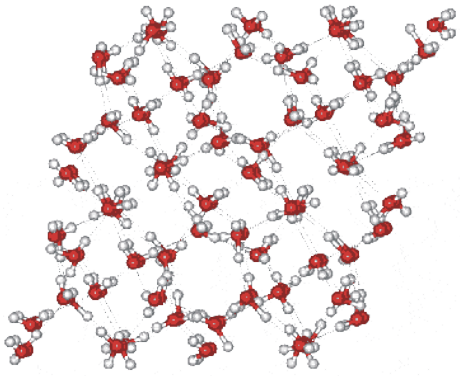
Ice-four (Ice IV)



Ice-four (ice IV) may be formed by the heating high-density amorphous ice at a slow (0.4 K min^{-1}) rate from 145 K and at a constant pressure of 0.81 GPa [386] (a faster rate, for example, 15 K min^{-1}, preferably produces ice-twelve). Ice-four is metastable within the ice-three, ice-five and ice-six phase space (see Phase Diagram). It forms a rhombohedral crystal (Space group $R\bar{3}c$, **167**; Laue class symmetry -3m1) with cell dimensions 7.60 Å (a, b, c; 70.1°, 70.1°, 70.1°, 16 molecules) [387]. In the crystal, all water molecules are hydrogen bonded to four others, two as donor and two as acceptor. The structure is formed from two interpenetrating networks of both puckered and flattish hexamers (these allow the inter-penetration) consisting of more strongly hydrogen bound water. [a]



The penetrating hydrogen bond is longer (2.921 Å) but these water molecules also possess three shorter hydrogen bonds (2.783 Å). The hydrogen bonds forming the flattish rings are also somewhat extended (2.876 Å). The networks are not entirely independent as three quarters of the water molecules have one weaker hydrogen bond to the other network (2.806 Å, 143°); the fourth type of hydrogen bond present. Hence, molecules fall into two unequal classes experiencing different molecular environments. Note that in this structural diagram the hydrogen bonding is ordered whereas in reality it is random [460] (obeying the 'ice rules': two hydrogen atoms near each oxygen,

one hydrogen atom on each O···O bond). Ice-four is one of only two disordered ice crystals (with cubic ice) where the ordered form has not yet been found.

Interactive Jmol structures are given.

Footnotes

[a] The hydrogen-bonded structure of ice-four has been questioned [403] but recent Raman spectra seems to support the structure presented here [460]. It may be that it is more stable as the deuterated ice. [Back]

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