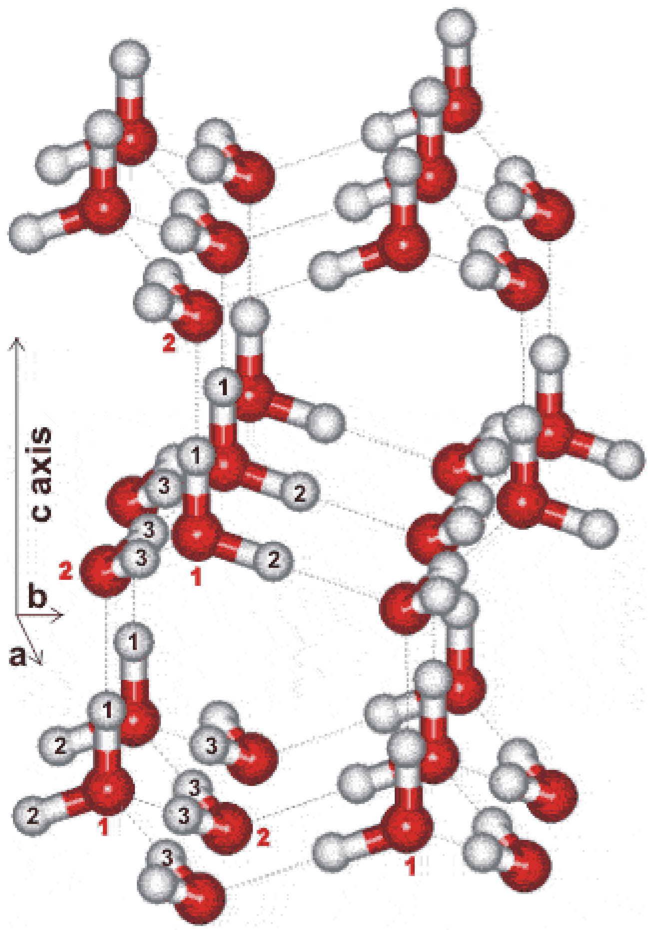
Ice-eleven (ice XI)

Water molecules in ice Ih are surrounded by four randomly directed hydrogen bonds. Such arrangements should change to an ordered (regular) arrangement of hydrogen bonds at low temperatures, so long as localized proton hopping is sufficiently enabled; a process that eases with increased pressure [1084]. Ice-eleven (ice XI) is the low-temperature equilibrium structure of hexagonal ice prepared from dilute KOH (10 mM) solution kept just below 72 K (at ambient pressure; D_2O 76 K) for about a week [207].[a] The low temperature of this transition has been correlated with the low energy difference between the most and the second most stable ice configurations [1655]. Ice XI can also be produced from a thin film (20 nm) of pure solute-free cubic ice (Ic) under electron beam irradiation [1924].



The hydroxide ions create defects in the hexagonal ice allowing protons to jump more freely between the oxygen atoms (and so this structure of ice XI breaks the 'ice rules'). The ions may also compensate for the large net dipole moment of the crystal lattice along the c-axis. A loss of entropy by proton ordering occurs to give a more stable structure (that is, about one sixth lower internal energy). The K^+ ions occupy interstitial sites in the hexagonal boxes but neither ion is shown in the structures given. Ice-eleven is the thermodynamically favored form of ice at atmospheric pressure at these low temperatures. It is a proton-ordered form of hexagonal ice forming orthorhombic crystals (Space group $Cmc2_1$, **36**;symmetry C_{2v} Laue class symmetry mmm). The unit cell has dimensions a

= 4.5019, b = 7.7978 c = 7.3280 (90º, 90º, 90º, 8 molecules) and is shown opposite [388]. Two oxygen (1:2 50:50) and three hydrogen positions (1:2:3 25:25:50) are nonequivalent (see labels opposite. Oriented bonds parallel to the c-axis give ferroelectric character (that is, they have a net dipole).The opposite orientation, of both molecules and dipoles, of alternating layers in the a-b planes gives rise to a small (~2%) relative displacements (middle layer to right, opposite).

There are distinct differences in the Raman spectra between ices 1h and XI, with ice XI showing much stronger peaks in the translational (~230 cm^{-1}), librational (~630 cm^{-1}) and in-phase asymmetric stretch (~3200 cm^{-1}) regions [1234].
As ice XI is thought to have the most stable conformation of ice Ih but the transfomation from ice Ih may be very slow, its structure has been sought, and found, in ancient antarctic ice 10^2 - 10^4 years old [798] and in other pure water samples [1636]. This study [798] indicated the transformation temperature (ice XI $\rightleftharpoons$ ice Ih) is -36ºC, which is far higher than the expected, but unobtainable, triple point (with hexagonal ice and water vapor) of KOH-catalyzed ice-eleven (~0 Pa, 71.6 K). Ice Ih that has once transformed to ice XI and back to ice Ih, on raising the temperature, retains some hydrogen-ordered domains and more easily transforms back to ice XI [1629].

Ice XI has a triple point with hexagonal ice and gaseous water (72 K, ~0 Pa).

It seems possible there may be a proton-ordered form of cubic ice (called ice XIc) [1753], but this has yet to be made.

Interactive structures of ice-eleven (Jmol) are available.

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