

X-RAY DETERMINATION OF THE STRUCTURE OF ICE IV

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ABSTRACT. Ice IV, a wholly metastable ice phase, has a structure based on a framework of tetrahedrally hydrogen-bonded water molecules in a rhombohedral unit cell. The structure involves two non-equivalent types of water molecules and four non-equivalent types of hydrogen bonds. A novel structural feature is a hydrogen bond that passes through the center of a 6-ring of water molecules and links non-adjacent structural layers. The bond network is proton-disordered, even after quenching.

RÉSUMÉ. *Détermination de la structure de la glace IV aux rayons X.* La glace IV, qui est une phase totalement métastable a une structure correspondant à un réseau de molécules d'eau liées à leurs voisines par des liaisons hydrogène respectant la symétrie tétraédrale et à une maille élémentaire rhomboédrique. Cette structure implique 2 types de molécules d'eau et 4 types de liaisons hydrogène. Le caractère structural original est dans le fait que des liaisons hydrogène passent à travers des anneaux de 6 molécules d'eau, reliant ainsi des couches non adjacentes. Il n'y a pas d'ordre protonique dans le réseau de liaisons, même après trempe.

ZUSAMMENFASSUNG. *Bestimmung der Struktur von Eis IV mittels Röntgenbeugung.* Eis IV, eine völlig metastabile Eisphase, besitzt eine Struktur, die auf einem Gerüst von tetraedrisch über Wasserstoffbrücken gebundenen Wassermolekülen in einer rhomboedrischen Elementarzelle beruht. Die Struktur verknüpft zwei ungleichwertige Typen von Wassermolekülen und vier ungleichwertige Typen von Wasserstoffbrückenbindungen. Ein neuartiges Strukturmerkmal ist eine Wasserstoffbrückenbindung, die durch den Mittelpunkt eines Sechsrings von Wassermolekülen hindurchgeht und nicht-aneinandergrenzende Lagen der Struktur verbindet. Das Bindungsnetzwerk ist in bezug auf die Protonen ungeordnet, selbst nach Abschreckung.

Ice IV is a polymorph of ice that has no field of true stability, being metastable with respect to ice V, ice VI, and ice III in the temperature and pressure range where it can be formed, namely *c.* 4 100 to 6 000 bar and -18 to -7°C (Engelhardt and Whalley, 1972).

Its structure has been determined and refined by least-squares methods using nearly-complete three-dimensional X-ray diffraction data from D_2O single crystals quenched to 77 K and released to atmospheric pressure.

The structure is based on a rhombohedral cell measuring $a = 760$ pm, $\alpha = 70.1^{\circ}$, and containing 16 water molecules. The density at atmospheric pressure and 110 K is 1.27 Mg m^{-3} , intermediate between that of ice V (1.23 Mg m^{-3}) and ice VI (1.31 Mg m^{-3}).

The space group for ice IV is $R\bar{3}c$. This is the same space group as that to which the ice II structure would transform upon disordering of its ordered proton arrangement. However, the actual structure of ice IV is quite different, being based on a topologically entirely different arrangement of water molecules and hydrogen bonds.

The structure is built from two symmetrically non-equivalent kinds of oxygen atoms, O(I) in general positions $12f$ of space group $R\bar{3}c$, and O(II) in special position $4c$, lying on the 3-fold axis. The atomic coordinates of the 16 oxygen atoms of the rhombohedral unit cell are given in Table I. The coordinates of O(2), O(3), ..., are related to those of O(1) by the symmetry transformations of space group $R\bar{3}c$, and the coordinates of O(14), O(15), ..., are similarly related to O(13).

The structure consists of water molecules hydrogen-bonded to one another in a tetrahedral bond framework. The most interesting element of the structure, shown in Figure 1, consists of a flat-puckered, hydrogen-bonded 6-ring of water molecules, through the center of which passes a hydrogen bond between two water molecules located above and below the 6-ring along the c_{H} -axis. In Figures 1 and 2, only the oxygen atoms of the water molecules are explicitly shown, the hydrogen atoms being implicitly indicated by the hydrogen bonds, which are represented by rods connecting the oxygen atoms. Oxygen atoms of type O(I) form the puckered 6-ring in Figure 1, while the pair of oxygen atoms lying on the 3-fold

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TABLE I. ATOMIC COORDINATES IN ICE IV IN FRACTIONAL UNITS OF THE RHOMBOHEDRAL AXES

Atom type	Atom	x	y	z
O(I)	O(1)	0.380	-0.110	-0.240
O(I)	O(2)	-0.240	0.380	-0.110
O(I)	O(3)	-0.110	-0.240	0.380
O(I)	O(4)	-0.380	0.110	0.240
O(I)	O(5)	0.240	-0.380	0.110
O(I)	O(6)	0.110	0.240	-0.380
O(I)	O(7)	0.260	0.390	0.880
O(I)	O(8)	0.880	0.260	0.390
O(I)	O(9)	0.390	0.880	0.260
O(I)	O(10)	0.740	0.610	0.120
O(I)	O(11)	0.120	0.740	0.610
O(I)	O(12)	0.610	0.120	0.740
O(II)	O(13)	0.085	0.085	0.085
O(II)	O(14)	-0.085	-0.085	-0.085
O(II)	O(15)	0.585	0.585	0.585
O(II)	O(16)	0.415	0.415	0.415

c_H -axis, and bonding to one another through the ring center, along the axis, are of type O(II). The situation depicted in Figure 1, in which a hydrogen bond between two water molecules threads through the center of a ring to which the two molecules are not bonded, occurs in modified form in ice V, where the threaded ring is an 8-ring (Whalley, 1976, p. 1447). This type of structural element represents bond interpenetration without interconnection, and presages the self-clathrate feature that occurs in the denser ice phases (Kamb, [c1968], p. 511).

The hydrogen bonds are of four non-equivalent kinds, of lengths (O-O distances) 279, 282, 288, and 290 pm. Because of the bond lengths, the H-bonds are asymmetric, the hydrogen atom in each bond lying approximately 100 pm from one end of the bond or the other. The arrangement of the protons in the H-bonds is probably disordered in the same sense as that in ice I (Pauling, 1960, p. 466). The bonds of lengths 279, 282, and 290 pm must be proton-disordered because of constraints of symmetry. The X-ray intensities suggest that the fourth bond, which is the type of bond forming the puckered 6-rings, is also disordered, but neutron diffraction data would be necessary to establish this with certainty. The O-O-O bond angles

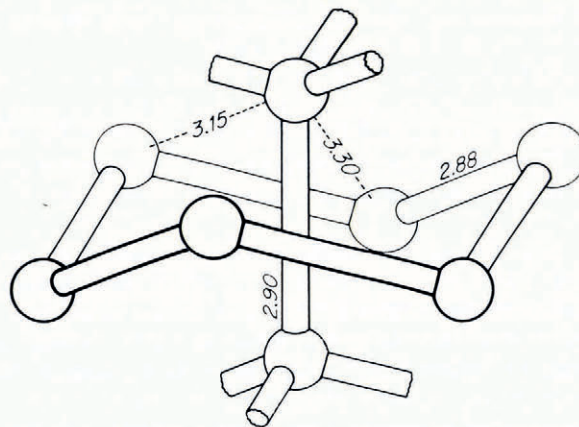


Fig. 1. The essential structural element of ice IV. Oxygen atoms of type O(I) form the puckered 6-ring. The balls represent oxygen atoms and the connecting sticks represent hydrogen bonds. Oxygen atoms bonded through the ring center are of type O(II). The numbers show the bond lengths and short non-bonded oxygen-oxygen distances, in ångströms. The hexagonal c_H axis is vertical, parallel to the H-bond between O(II)-type atoms.

formed by O(I) as apex atom range from 87.7° to 127.8° and those by O(II) from 91.8° to 124.0° , so that the bonding is substantially distorted from ideal tetrahedral geometry.

Figure 2 shows the structure of ice IV as viewed nearly perpendicular to the hexagonal c_H -axis, this axis being tilted 10° out of the plane of the drawing. The numbering of the atoms in Figure 2 is the same as in Table I. Molecular groups of the kind shown in Figure 1 can be seen, and the lateral interconnections among these groups are also visible.

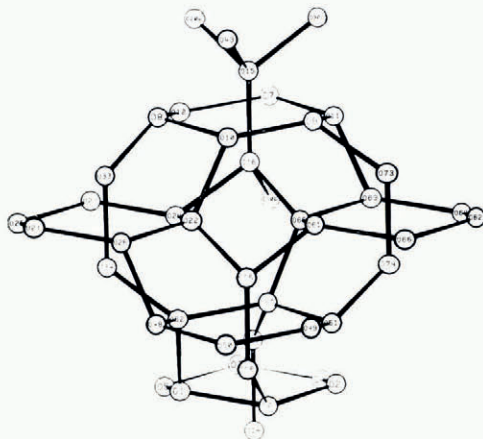


Fig. 2. Structure of ice IV. The hexagonal c_H axis is oriented vertically and is tilted about 10° from the plane of the paper. Oxygen atoms O(1) to O(16) are the atoms listed in Table I and represent the contents of the rhombohedral unit cell. Five structural units of the type shown in Figure 1 are depicted in this diagram. The pairs such as O(15)–O(16) are pairs of O(II)-type atoms bonded parallel to the c_H axis. Groups such as O(1)–O(6) and O(7)–O(12) are puckered 6-rings of O(I)-type atoms.

The molecular arrangement in ice IV can be interpreted as a layer structure related in a somewhat circuitous way to ice Ic (low-pressure cubic ice). In the sense of this relationship, the bonds between pairs of O(II) atoms, passing through the 6-rings, are in fact bonds between non-adjacent layers (second-neighbor layers), rather than between immediately adjacent layers. This feature is very unusual, indeed perhaps unique, for a layer structure.

ACKNOWLEDGEMENT

We thank Peter Pauling for providing the computer drawing of the structure of ice IV shown in Figure 2.

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DISCUSSION

J. BERTIE: Have any significant spectroscopic measurements been made on ice IV?

E. WHALLEY: Some years ago Dr Engelhardt measured the infrared spectrum of ice IV in Ottawa. The main conclusion was that, to the precision of the technique, the water molecules have fully disordered orientations.