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Neutron-Diffraction Study of Ice Polymorphs. II. Ice II*

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Neutron-diffraction spectra have been obtained at 80°K for polycrystalline D_2O ice II prepared from ice Ih at 3 kbar and 195°K. An analysis of the 55 peaks in the 2θ diffraction angle between 10° and 57.3° has been made. The results of this study are in accord with the existence of a proton-ordered arrangement for this ice as proposed by Kamb. Ice II has a rhombohedral unit cell with lattice parameters $a_R = 7.743 \pm 0.002$ Å, $\alpha_R = 113.09 \pm 0.03°$. Indexed on the triply primitive hexagonal cell, ice II has the parameters $a_H = 12.920 \pm 0.003$ Å and $c_H = 6.234 \pm 0.002$ Å at 80°K. The transformation of ice V to ice II by decompression at −35°C, an alternate way of forming ice II, has been observed to be slow. Although the O–O–O bonds in ice II are appreciably distorted from the tetrahedral arrangement found in ice Ih, the computer-refined position parameters for the deuterons indicate that the D–O–D angles are 106°±3°. These results support the existence of bent hydrogen bonds in ice II.

INTRODUCTION

Ices II and IX were recovered by Tammann[1] in a metastable state at atmospheric pressure by quenching the samples in liquid nitrogen before releasing the pressure required for their formation. This procedure has been of inestimable value in simplifying the experimental requirements for the study of the high-pressure forms of ice. The current work is part of a program to determine, with the methods of neutron diffraction, the lattice parameters as well as the proton and oxygen positions in a number of the ice polymorphs. In the first paper of this series,[2] the structure of ice IX was examined. Ice II is clearly set apart from ices Ih, III, V, and VI, for example, by its lack of dielectric dispersion[3,4] and its residual entropy.[5] This entropy, which has been associated with proton ordering in this ice, has been shown[6] to be 0.77 cal $deg^{-1} \cdot mole^{-1}$ less than that for ice Ih between −35° and −75°C from the results of Bridgman[7] on the thermodynamic properties related to the ice I–ice II phase boundary. These results, together with the narrowness of the ν_{OH}(HDO) and ν_{OD}(HDO) peaks in the infrared spectrum[8] of ice II, provide strong support for a proton-ordered structure for this polymorph.

Single-crystal specimens of ice II have been examined by Kamb[6] with x-ray methods, and although it is not possible to establish proton positions by this procedure in a direct fashion, he was able to infer a proton-ordered arrangement for this ice on the basis of structural considerations. A space group $R\bar{3}$ was assigned to ice II [6] with 12 molecules in the rhombohedral unit cell.

X-ray powder patterns of ice II have been reported by Bertie *et al.*[9] with the parameters $a_H = 12.92$ Å, $c_H = 6.23$ Å if the spectrum is indexed on the hexagonal unit cell. From a study of the transformation properties of ice II to ice Ic, these authors concluded that this rate of transformation was temperature dependent.

Nuclear magnetic resonance studies which have been conducted on ice II [10] have indicated that the protons are not located along the line of the oxygen–oxygen bonds, but instead are more nearly positioned at the angle of 104.5° which is found for the H–O–H angle in the vapor phase.[11] The present neutron-diffraction work on ice II provides additional support for this proton arrangement.

EXPERIMENTAL

Ice II was prepared following the procedure of Bridgman[7] described by Bertie *et al.*[9] Ice Ih (99.8% D_2O) was subjected to a pressure of about 1 kbar in a heat-treated $\frac{3}{8}$-in.-i.d. Be–Cu pressure vessel described previously.[2] After the ice Ih sample attained thermal equilibrium in a solid CO_2–acetone bath, the pressure was raised to about 3 kbar. The transformation did not occur rapidly as judged by the rate of piston displacement. Pressure was maintained at the 3-kbar level for about $\frac{1}{2}$ h, and at the end of this time, the sample temperature was raised to −40°C and held for 40 min at this value with an ethylene glycol–water bath. Although some transformation of ice Ih to ice II probably occurred at −78°C, it was evident that the major portion of the sample transformed as the sample was warmed to −40°C. Finally, the sample under pressure was quenched in liquid nitrogen and ejected

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