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 $a_R = 7.743\pm0.002$ Å, $\alpha_R = 113.09\pm0.03°$. Indexed on the triply primitive hexagonal cell, ice II has the parameters $a_H = 12.920\pm0.003$ Å and $c_H = 6.234\pm0.002$ 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·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 $\nu_{OH}(HDO)$ and $\nu_{OD}(HDO)$ 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 struc-

tural 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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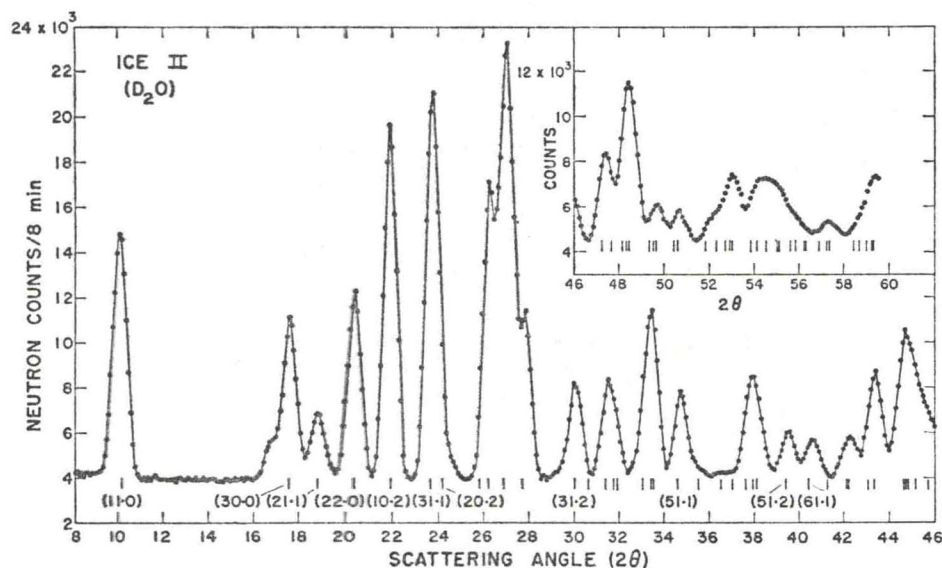[11] W. S. Benedict, N. Gailar, and E. K. Plyler, J. Chem. Phys. 24, 1139 (1956).

from the pressure vessel. Because it has been reported that if the temperature is much above −78°C ice III can form from ice Ih even in the region where ice II is the stable phase,[1,7] it was necessary to try to obtain confirmation that ice II was indeed the product of the transformation. This was in part accomplished by an experimental determination of the density of H_2O ice by measuring the buoyant force exerted on the coarsely divided powder as it was immersed in liquid nitrogen (later confirmed by neutron diffraction results). The ice was suspended at the end of the beam of an analytical balance with a fine wire supporting a glass vial immersed in a Dewar of liquid nitrogen. The experimental value of the ice II density was within 1% of the calculated value[6] of 1.17 g cm^{-3}. It must be pointed out that the use of density as a means of distinguishing between ices II and III is somewhat marginal because of the rather small difference in the density which is found for these ices. Ice III (equivalent to ice IX) has a density of 1.14[12] g cm^{-3}.

A procedure has been described[4] for the preparation of ice II by the decompression of ice V at −35°C. As suggested in this method, liquid water was cooled to −35°C under a pressure of 5 kbar. After ice V formed, the pressure was lowered to about 3 kbar and held at this value for about 1 h. Upon examination of the quenched sample in the neutron diffractometer, it was determined that ice II had not formed, but instead, a spectrum corresponding to that of ice V was obtained. The rate of transformation of ice V to ice II has not been exhaustively examined. Since Wilson et al.[4] have reported the formation of ice II in this way, and suggest it as a more convenient way than the compression of ice Ih, we simply wish to point out that under some circumstances the rate of transformation of ice V to ice II may be slow.

12 W. B. Kamb and S. K. Datta, Nature 187, 140 (1960).

The grinding of the powdered ice and loading of the neutron-diffraction sample holder under liquid nitrogen, as well as the characteristics of the neutron diffractometer and its calibration, have been described previously.[3]

EXPERIMENTAL RESULTS

The neutron-diffraction spectrum of polycrystalline D_2O ice II obtained at 80°K is shown in Fig. 1. As described in the Experimental section, the ice II was made by the transformation of ice Ih under pressure. Hexagonal ice was present as an impurity of at most a few percent. This is shown by the appearance of weak peaks at diffraction angles of 2θ equal to approximately 16.8° and 29.4°. The presence of these peaks is indicated as much by the asymmetry which they impart to the nearby ice II peaks as by their own intensities. Not only is it logical to expect the impurity to be ice Ih since the ice II was made by the transformation of this ice, but also the positions of the lines can be indexed as (100) and (110) hexagonal-ice peaks. These are lines of major intensities in the hexagonal-ice spectrum. Because the peak intensities, centroids, and half-widths of the lines in the hexagonal ice spectrum had been determined in this work under similar experimental conditions, it was possible to subtract the contribution of an amount of hexagonal ice which would produce the expected Gaussian line shape for the (300) ice II peak. This hexagonal-ice background was subtracted throughout the entire range of 2θ covered to obtain the corrected ice II diffraction pattern. From the care which was taken to keep the ice II sample at or within a few degrees of liquid-nitrogen temperature during the grinding and loading operations, as well as during the spectrum-recording period, it appears that the hexagonal ice which was present in the sample was not the result of the transformation of ice II to the hexagonal form. Since the ice II was made by the phase trans-

formation of ice Ih, it has been considered that the impurity of hexagonal ice represents the small amount which did not transform under the experimental conditions employed. Perhaps a period of about 1 h at $-40°C$ might be a more appropriate length of time to allow for the phase transformation if it is desired to essentially eliminate small amounts of hexagonal ice from the sample.

Kamb[6] has pointed out that the unit cell of ice II is rhombohedral. There are 12 water molecules in the unit cell with the oxygen atoms located in two sets of six equivalent positions. Two six-membered rings of oxygen atoms similar to those found in ices Ih and Ic are present; in one the atoms are nearly planar, and in the other there is considerable puckering. In the larger hexagonal cell there are 36 molecules with the oxygens in two sets of 18 equivalent positions.

A Gaussian line-fitting procedure which has been described in a previous study[2] was used to obtain the peak centroids, intensities, and half-widths for the 55 ice II peaks in the 2θ range between 10° and 57.3°. The results are listed in Table I. As indicated, centroid posititons of the weaker peaks were held fixed at the values calculated from the cell lattice parameters in order that a more reliable estimate of their intensities could be made.

Values of the rhombohedral lattice parameters obtained in this work are $a_R=7.743\pm0.002$ Å, $\alpha_R=113.09°\pm0.03°$. For the corresponding hexagonal cell, the parameters are $a_H=12.920\pm0.003$ A and $c_H=6.234\pm0.002$ Å. These results are in excellent agreement with the values reported by Bertie et al.[9] In Fig. 1, the centroids of the peaks which were calculated on the basis of these lattice parameters are marked with short vertical lines above the indicated hexagonal indices. Only the more prominent peaks have been indexed in the figure.

An ordered-proton arrangement in ice II has been suggested[5,6] on the basis of dielectric relaxation and residual entropy considerations and infrared and x-ray spectra. There are four nonequivalent hydrogen atoms in the ice II lattice. The coordinates of these atoms together with the positions of the two nonequivalent oxygen atoms given in Table II represent the initial estimate of the spatial arrangement of the atoms. Since the oxygens had been located with such a high degree of precision, no attempt was made to further refine these positions. To simplify calculations in this work, hexagonal coordinates have been used throughout. Rhombohedral coordinates[6] were transformed to hexagonal coordinates with the appropriate transformation matrices.[13]

In the initial estimate of the deuteron coordinates which are given in Table II, each O–D bond distance was chosen to be 1.01 Å as is found in ice Ih. In the selection of the D–O–D bond angles, one choice would

[13] International Tables for X-Ray Crystallography, K. Lonsdale et al., Eds. (Kynoch Press, Birmingham, England, 1962), Vol. 2.

TABLE I. Neutron-diffraction line centroids and intensities in ice II at 80°K.

		Experimental		Calculated
hkl	$2\theta°$	$I_0\pm\sigma$		I_a
110	10.12	8.29	0.11	8.00
101	Fixed	0.00	0.20	0.00
021	Fixed	0.00	0.20	0.08
030	17.61	4.55	0.07	4.47
211	18.79	1.52	0.06	1.62
220	20.37	5.67	0.14	5.45
012	21.92	10.53	0.17	10.38
131	23.73	11.03	0.27	10.68
202	24.10	1.78	0.55	1.26
401	Fixed	0.00	0.09	0.20
122	Fixed	9.17	0.21	9.44
410	27.08	12.81	0.20	13.25
321	Fixed	4.81	0.20	5.03
312	30.11	2.94	0.10	2.93
330	30.76	0.03	0.20	0.01
051	Fixed	2.30	0.15	2.27
042	Fixed	0.15	0.50	0.16
003	Fixed	1.00	0.50	1.28
241	Fixed	1.50	0.16	1.98
232	Fixed	3.94	0.80	4.14
113	Fixed	0.57	0.72	1.21
511	34.77	2.65	0.10	2.67
600	Fixed	0.14	0.20	0.26
502	Fixed	0.19	0.20	0.22
033	Fixed	0.05	0.20	0.02
250	Fixed	0.09	0.20	0.09
431	Fixed	1.99	0.20	2.03
422	Fixed	1.53	0.90	1.77
223	Fixed	0.44	0.80	0.15
152	Fixed	1.54	0.05	1.56
161	Fixed	1.29	0.05	1.27
440	Fixed	0.03	0.80	0.01
342	Fixed	0.96	0.80	0.75
413	Fixed	0.31	0.86	0.79
351	Fixed	1.48	0.39	1.37
104	Fixed	1.96	0.36	2.74
621	Fixed	2.86	0.40	3.60
024	Fixed	0.36	0.40	0.51
612	Fixed	0.95	0.50	1.87
333	Fixed	0.55	0.34	0.44
170	Fixed	2.30	0.34	2.18
214	Fixed	1.41	0.20	1.55
532	Fixed	3.16	0.20	3.70
630	Fixed	0.16	0.14	0.20
541	Fixed	1.60	1.50	2.33
134	Fixed	2.00	1.50	3.06
262	Fixed	0.07	0.25	0.29
063	Fixed	2.66	1.50	2.30
081	Fixed	0.06	0.50	0.17
404	Fixed	0.50	0.75	0.74
523	Fixed	1.00	1.00	1.74
271	Fixed	0.75	0.50	0.74
324	Fixed	0.51	0.50	0.92
452	Fixed	0.92	0.60	1.13
550	Fixed	0.39	0.34	0.58

TABLE II. Initial position parameters for oxygen and deuterium atoms in ice II.

Atom	x	y	z
H(I 2)	0.154	0.204	0.992
H(I 4)	0.221	0.207	0.210
H(II 1)	0.221	0.108	0.510
H(II 3)	0.306	0.072	0.437
O_I	0.222_7	0.196_3	0.050_3
O_{II}	0.188	0.230	0.480

have been to place the deuterons along the O–O bonds even though the O–O–O bond angles are 88° and 99°. However, second-moment proton NMR measurements[10] of ice II have strongly suggested an O–D bond length near 1.01 Å and an H–O–H angle of near 105°. Also, the work of Chidambaram[14] has conclusively demonstrated that in the case of hydrogen-bonded water molecules in a variety of crystals, even though the X_1–O–X_2 angle departs significantly from the tetrahedral angle, the bonding of the water molecule in the X_1–H–O–H–X_2 configuration is such as to give rise to an H–O–H angle close to the tetrahedral angle. Accordingly, both the H(I 2)–O_I–H(I 4) and the H(II 1)–O_{II}–H(II 3) angles, following the atom-designation system used in Kamb's paper,[6] were placed at initial values of 105°.

The refined deuteron atom-positioned parameters for ice II are given in Table III. These were obtained by a least-squares computer program which minimized the quantity $\sum w(I_0-I_c)^2$, where I_0 and I_c are the observed and calculated peak intensities, respectively, and w is a weighting factor proportional to the reciprocal square of the standard deviation of I_0. The atom positions in Table III, together with the oxygen positions given in Table II, can be used to calculate the water-molecule configurations shown in Table IV.[15]

DISCUSSION

A comparison of the initial and computer-refined deuteron-atom positions given in Tables II and III,

TABLE III. Refined-position parameters for deuteron atoms in ice II.[a]

Atom	x	y	z
H(I 2)	0.151±0.003	0.200±0.002	0.983±0.006
H(I 4)	0.223±0.002	0.214±0.003	0.202±0.005
H(II 1)	0.219±0.002	0.112±0.002	0.517±0.004
H(II 3)	0.302±0.002	0.065±0.002	0.442±0.006

[a] The isotropic thermal parameter B was found to be 0.70 Å²; all atoms were constrained to have the same value.

[14] R. Chidambaram, J. Chem. Phys. 36, 2361 (1962).
[15] A. C. Larson, R. B. Roof, Jr., and D. T. Cromer, "An Integrated Series of Crystallographic Computer Programs. VII. Interatomic Distances and Angle Calculations," Los Alamos Scientific Lab. Rept. LA-3309 (1965).

respectively, shows that only small displacements of the deuterons from the initially selected values were required. The residual R was found to be 0.041, where R is defined by the ratio $\sum_i w_i\,|\,I_0-I_c\,|/\sum w_i I_0$. This excellent quality of the fit suggested that any additional adjustment of the oxygen positions was not warranted. Kamb's oxygen positions were obtained by an x-ray analysis[6] of single crystals of ice II and the standard deviations of the oxygen coordinates were reported to be close to 0.0010.

It is of considerable interest to observe that for the ice II lattice, evidence has been obtained which supports the existence of bent hydrogen bonds. Yet, judging from the NMR results,[10] there is no great difference in the hydrogen-bond strengths of the various ice polymorphs. The O_I–D and O_{II}–D bond distances have been shown by an analysis of the neutron-diffraction spectrum to be very close to 1.00 Å.

As pointed out in the Introduction of this paper, strong support for proton ordering has been provided in previous work on the basis of infrared, dielectric relaxation, and residual entropy considerations. To

TABLE IV. Water-molecule configurations for nonequivalent oxygens in ice II.

Molecule	Bond distances and angles	
O_I	H(I 2)–O_I	1.04±0.04 Å
	H(I 4)–O_I	0.98±0.03 Å
	H(I 2)–O_I–H(I 4)	106±3°
O_{II}	H(II 1)–O_{II}	0.98±0.03 Å
	H(II 3)–O_{II}	0.96±0.04 Å
	H(II 1)–O_{II}–H(II 3)	106±3°

these can now be added the additional fact that neutron-diffraction measurements of polycrystalline D_2O ice are in accord with a proton-ordered arrangement.

Bertie and Whalley[8] have discussed the reasons for the existence of proton order in ice II when the ices Ih and Ic, for example, do not show this preferential atom positioning. Their suggestion was that the O–O'–O angles will in general be different and the hydrogen atoms bound to an O' will seek the minimum potential-energy configuration. In view of the data obtained in the present work on atom positions, it appears that this is precisely the case. In ices Ih and Ic there is not enough difference in the various O–O–O bond angles to permit one proton orientation to be particularly favored energetically, and consequently, these are proton-disordered arrangements.

The fact that ice II was not produced by the decompression of D_2O ice V at $-35°C$ most probably is associated with the slower rate of transformation of D_2O ice at this temperature. The description[4] of the method was outlined for H_2O ices. Typically, the phase diagram of the D_2O ices corresponds to that for the H_2O ices with the difference that at a given pressure

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the deuterium solid phases exist at higher tempera-
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to 12 ml of powdered ice was needed. Five separate
samples of D_2O ice V were prepared by cooling the

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[16] P. W. Bridgman, J. Chem. Phys. **3**, 601 (1935).

liquid at 5 kbar to −35°C, lowering the pressure to
3 kbar after ice V had formed, and holding the sample
at this pressure for 1 h at this temperature. It appears
that the rate of transformation must be slow under
these conditions for D_2O since a single ice V phase was
indicated by the neutron-diffraction spectrum of the
combined samples treated in this fashion.

Neutron-Diffraction Study of Ice Polymorphs. III. Ice Ic*

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Neutron-diffraction spectra have been recorded at 80°K for polycrystalline D_2O cubic ice (Ic) obtained
by the transformation of the high-pressure ices II, V, and IX. Spectral differences were found among these
ice Ic preparations, principally in the degree of asymmetry of the (111) cubic reflection and in the extent
of line broadening. The cubic (111) peak of greatest symmetry was obtained by the transformation of ice
II. The line broadening appears to be associated with the small particle sizes of the ice Ic produced by
the transformation of the high-pressure ices under controlled-temperature conditions. Peak centroids for
scattering angles between 15° and 62° give a weighted cubic lattice parameter, $a_0 = 6.353 \pm 0.001$ Å. As
revealed by an analysis of neutron-diffraction line intensities, attempts to induce the formation of ice Ic
by the quenching of aqueous ferrous chloride or potassium chloride solutions in liquid nitrogen were un-
successful.

INTRODUCTION

Neutron-diffraction studies of cubic ice (Ic) have
been made in this work to supplement investigations
made on this form of ice by electron-diffraction,[1-4]
x-ray,[5,6] and nuclear magnetic resonance methods.[7]

In addition to ordinary hexagonal ice (Ih), ice Ic
and vitreous (or amorphous[8]) ice can be prepared by
the condensation of water vapor at low temperatures.
The particular form which is produced is dependent
upon the temperature of deposition. Ice Ic can be pre-
pared between −120° and −140°C, while vitreous ice
requires temperatures of −160°C or below.[6] Bertie
et al.[9] have demonstrated that the high-pressure ice
polymorphs first transform to ice Ic as they are warmed
at atmospheric pressure from the metastable quenched
condition at 77°K. These authors suggest that large

amounts of ice Ic can be conveniently prepared by the
conversion of ice IX at 156°K for a minute or two.

Nozik and Kaplan[10] have reported that aqueous
solutions of ferrous sulfate and of ferrous chloride which
have been quenched in liquid nitrogen induce the
formation of ice Ic rather than ice Ih. Their conclusion
was based on changes observed in the two-line Möss-
bauer spectrum characteristic of a nuclear quadrupole
hyperfine interaction in ^{57}Fe. Weltman[11] has reported
that ice Ic was prepared along with ice Ih by quenching
$0.04N$ and $0.4N$ aqueous KCl solutions in liquid nitro-
gen. The ices were identified by their x-ray patterns.

The oxygen atoms in ice Ic are arranged in puckered-
hexagonal rings identical to those found in ice Ih;
however, each layer of oxygens is displaced one-half the
diameter of the ring relative to adjacent layers. This
arrangement gives rise to a repetitive structure of the
type ···ABCA··· characteristic of the diamond-cubic
system. The infrared[12] and Raman spectra[13] of ices Ih
and Ic are identical in the O–H stretching region. Both
infrared[12] and electron-diffraction results[3] have been
interpreted as indicating a disordered-proton arrange-
ment in ice Ic.

Dowell and Rinfret[6] have obtained the cubic lattice

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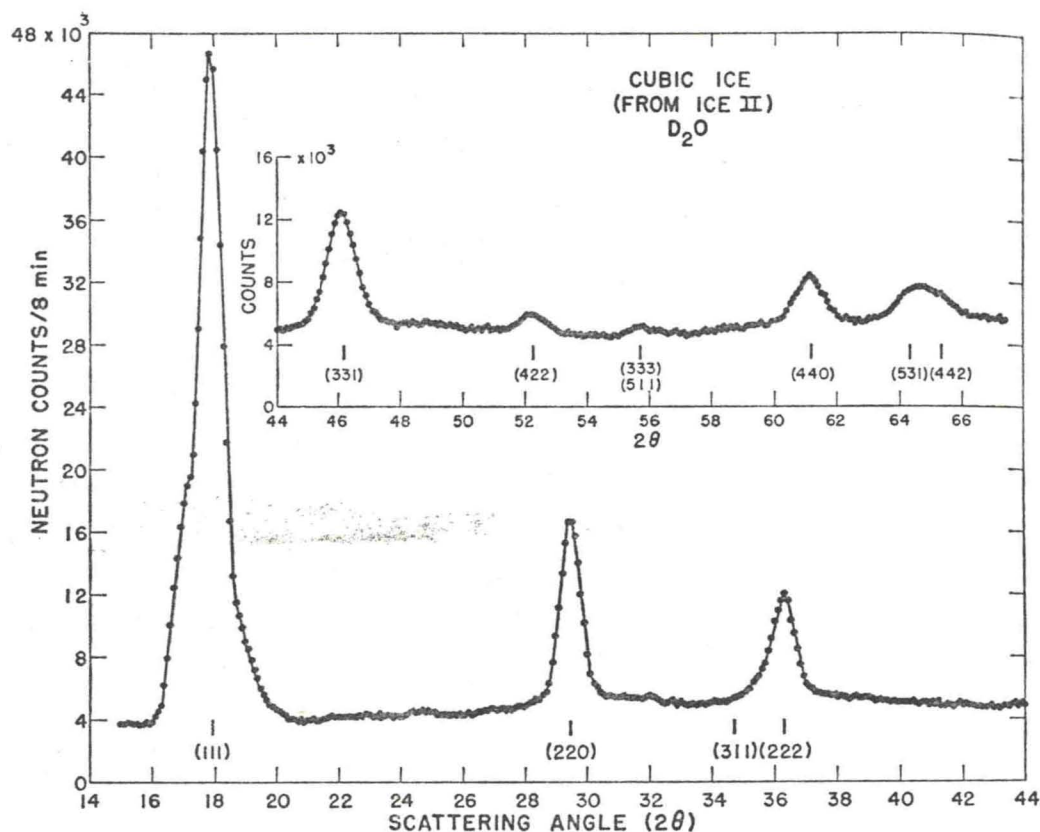[13] M. J. Taylor and E. Whalley, J. Chem. Phys. **40**, 1660
(1964).

FIG. 1. Neutron-diffraction spectrum of ice Ic at 80°K prepared from ice II.

parameter $a_0 = 6.358 \pm 0.004$ Å at $-185°C$ from x-ray studies of polycrystalline material. With eight molecules in the unit cell, this lattice dimension (with the latest values of the fundamental constants) leads to a calculated density of 0.931 g-cm^{-3} which is identical within experimental error to that of ice Ih.[14]

EXPERIMENTAL

Although ice Ic can be prepared by the low-temperature deposition of water vapor, only relatively small quantities can conveniently be prepared in this manner. Since about 10 g of ice were needed for a neutron-diffraction sample, use was made of the fact that all high-pressure ices first transform to ice Ic.[9] The high-pressure ices II, V, and IX were prepared in the Be–Cu pressure vessel described previously,[15] and transformed to the cubic form for this study. Because of the large spin-incoherent neutron scattering of protons, it was necessary to use D_2O samples to achieve spectra with acceptable peak-to-background ratios. The temperatures at which the transitions were made were 166°K for ices V and IX, and 177° for ice II. A liquid-nitrogen-cooled n-pentane bath was used. Some of the transfor-

mations were made in small glass bottles placed direc[t] in the constant-temperature bath, but none of the [..] were in direct contact with the n-pentane. In other ca[se..] the Ti–Zr neutron-diffraction sample-holder lid w[..] unscrewed to allow for the expansion of one of the hi[gh] pressure ices, and this container was placed in an ope[n] topped, thin-walled copper sleeve immersed in t[he] n-pentane bath. The sample temperature was monit[or..] with a copper–constantan thermocouple.

Neutron-diffraction spectra of liquid-nitrog[en] quenched solutions of $FeCl_2$ and KCl were taken [to] examine the reported induced formation[10,11] of ice I[.] Analytical-grade reagents were used to make the 0.4[N] $FeCl_2$ and 0.4N KCl solutions in D_2O. Droplets of [1] mm in diameter were dispensed from a capillary tip a[nd] quenched in liquid nitrogen. These small ice pellets w[ere] ground in a polished steel mortar under liquid nitrog[en.] This same procedure had been used in the samp[le] preparation of the high-pressure ices without bring[ing] about a phase change. The powdered ice was transferr[ed] to the sample holder under liquid nitrogen.

A characteristic feature in the preparation of ice I[c] is that the pure cubic phase is not formed by any of the reported methods. This appears to be true for the low temperature deposition of water vapor[5] and for th[e] transformation of both vitreous ice[6] and the high pressure ices.[12] The impurity in the cubic-ice sample ha[s]

[14] S. W. Rabideau, E. D. Finch, G. P. Arnold, and A. L. Bowman, J. Chem. Phys. 49, 2514 (1968), Paper I of this series.
[15] E. D. Finch, S. W. Rabideau, R. G. Wenzel, and N. Nereson, J. Chem. Phys. 49, 4361 (1968), Paper II of this series.

been suggested to be hexagonal ice. In the transformation of vitreous ice, a residual of this form was stated to be present, in addition to the ice Ih impurity.

The powder-diffraction spectra were obtained on a neutron diffractometer at the Los Alamos Omega West Reactor. The calibration, resolution, and operation of the diffractometer have been described in Paper I of this series.[15]

EXPERIMENTAL RESULTS

The neutron-diffraction spectrum obtained at 80°K by the transformation of ice II is shown in Fig. 1. The cubic cell lattice parameter, a_0, was found to be 6.353 ± 0.001 Å by an analysis of the centroids of the first seven peaks at scattering angles (2θ) between 15° and 62°. The calculated positions for this value of a_0 are indicated by the vertical lines placed above the (hkl) symbols in Fig. 1.

As indicated previously,[15] the angular accuracy of the neutron diffractometer and the dispersion were checked with the use of a standard sample of NbO, so that it was possible to determine the extent to which a given line in the ice Ic pattern was broadened.

The asymmetry of the (111) peak in the ice Ic spectrum of Fig. 1 is apparent. In addition to the shoulder on the low-angle side of this peak centroid, there is also broadening throughout the peak with a suggestion of an incipient peak in the region of $2\theta=19°$. All remaining lines in the spectrum, while reasonably symmetric, are appreciably broadened.

Essentially the same type of diffraction pattern was obtained from the samples prepared by the transformation of ices V and IX. The portion of the spectrum for a scattering angle 2θ of 16° to 20° is shown in Fig. 2. The ice Ic obtained from ice IX shows evidence for a shoulder on the high-angle side of the peak of major intensity, and a clearly resolved peak on the low-angle side. Although the heats associated with the transformations of ices V and IX to ice Ic are only 4 and 11 cal/g, respectively,[12] the possible contributions of these heats to the nature of the final ice Ic product was examined. Approximately 10 g of ice were needed for the neutron-diffraction pattern. In one case, the entire 10-g sample of ice V was placed in a glass bottle and transformed to ice Ic in the constant-temperature n-pentane bath. In a second trial, the sample of ice V was divided into six batches of approximately 1½ g and the transformation of each batch was made separately at 166°K. Since there was no detectable difference between the neutron-diffraction spectra obtained in these two ways, it was concluded that the transformation heats contributed little or nothing to the asymmetries observed under the conditions of these experiments.

In an attempt to try to resolve peaks of ice Ic obtained from ice IX into a series of component lines, Fig. 2, use was made of a Gaussian line-fitting program. However, even with as many as six lines in the 2θ region between
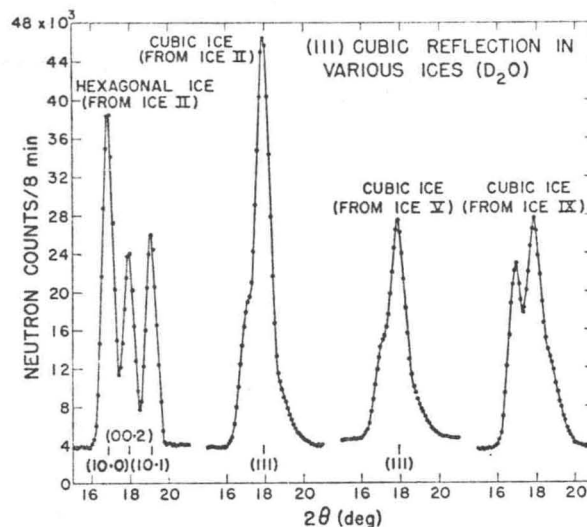

FIG. 2. Composite neutron-diffraction spectrum recorded at 80°K. Ice Ih prepared from ice II, ice Ic made by the transformation of ices II, V, and IX.

16° and 20°, the full widths at half-heights of the peaks were greater than would have been expected from the diffractometer dispersion characteristics. The spectrum of ice Ic from ice II was used for further analysis since this pattern had the most symmetric peaks.

The analysis of the spectrum pattern of ice Ic is made difficult by the presence of hexagonal ice. There are no lines in the cubic pattern that are not also found at essentially identical positions for ice Ih. To be able to determine the appropriate values to be subtracted from an observed possible mixture of ices Ic and Ih, peak intensities, half-widths, and centroids were obtained for ice Ih for the triplet peaks in the portion of the spectrum between 16° and 20°. For ice Ih prepared by the transformation of ice II at −50°C, the half-widths were found to be in accord with expected values for this instrument in this spectral region. Hexagonal indices are indicated for this triplet in Fig. 2. Ice II, prepared as described in Paper II of this series,[16] contained approximately 5% ice Ih. The contribution of this ice Ih impurity to the ice Ic spectrum was subtracted prior to attempting an analysis of the observed ice Ic spectrum. The residual peak widths were considerably in excess of those expected. These excess widths have been interpreted as arising from the small particle sizes of the ices which resulted from the ice II transformation. Although ice Ic was the principal product of this transformation, it appears that a small, additional amount of ice Ih was also formed.

In a series of Mössbauer studies of ferrous ions trapped in ice by the quenching of aqueous ferrous ion solutions in liquid nitrogen, Nozik and Kaplan[10] give convincing evidence for the induced formation of cubic ice. It was of interest to determine whether any evidence could be obtained by neutron-diffraction studies for

[16] R. Brill and A. Tippe, Acta Cryst. 23, 343 (1967).

TABLE I. Neutron-diffraction centroids, widths, and intensities of peaks in pure and in doped ices.

Sample	Peak	Centroid	Width[a]	Intensity
A. Pure hexagonal ice	(10·0)	16.85°	0.68°	1.00
	(00·2)	17.94	0.65	0.54
	(10·1)	19.11	0.67	0.59
B. Ice doped with	(10·0)	16.86	0.67	1.00
0.47M FeCl$_2$	(00·2)	17.94	0.64	0.54
	(10·1)	19.11	0.69	0.62
C. Ice doped with	(10·0)	16.83	0.67	1.00
0.40M KCl	(00·2)	17.94	0.65	0.50
	(10·1)	19.10	0.67	0.55

[a] Full width at half-maximum.

the presence of even relatively small amounts of cubic ice. As indicated by the results in Table I, the triplet peaks in the hexagaonal ice spectrum were obtained for pure ice Ih, for ice doped with 0.47M FeCl$_2$, and for ice prepared by quenching 0.40N KCl. The doped-ice-peak positions were not significantly altered from those of pure ice and the measured half-widths were in agreement with expected values on the assumption of no line broadening. The relative intensities were referenced on the (10·0) peak and were obtained from the relation $I=1.064 (\Delta H_{1/2}) Y_m$, where I is the intensity, $\Delta H_{1/2}$ is the full width at half-height, and Y_m is the peak height. Although the intensities of the peaks are not identical in the three ices, the differences in the ratios are small. A significant amount of ice Ic mixed with the hexagonal form would have been revealed by the alteration of the relative intensities of these peaks as well as by a displacement of the peak centtroids.

Lattice cell parameters have been obtained for polycrystalline D$_2$O ice Ih at 80°K from an analysis of the neutron-diffraction spectrum, a portion of which is shown in Fig. 2. The values which have been obtained are $a_0 = 4.500 \pm 0.001$ Å and $c_0 = 7.324 \pm 0.002$ Å. These results are in excellent agreement with the recent precise x-ray measurements of H$_2$O ice Ih reported by Brill and Tippe.[14] These lattice parameters give densities of 0.932 g cm^{-3} and 0.933 g cm^{-3} for H$_2$O ice Ih and ice Ic at 80°K, respectively, assuming that there is no difference in cell dimensions for the H$_2$O and D$_2$O ices.

DISCUSSION

The line centroids of the peaks in the ice Ic neutron-diffraction spectrum shown in Fig. 1 are in good accord with the calculated line positions based on a cubic cell lattice parameter, $a_0 = 6.353$ Å. Several features of the spectrum require comment, however. The obvious asymmetry of the (111) peak suggests that an impurity is present, and ice Ih would seem to be a likely possibility. The presence of ice Ih as an impurity would not be surprising, since it appears that pure ice Ic has not been prepared previously, and hexagonal ice has been considered to be the contaminant. If the line on the

low-angle side of the (111) cubic reflection is assigned to the (10·0) line in ice Ih (see Fig. 2), its intensity may be used to calculate the intensity to be expected for the (10·2) line. This results in an expected counting rate for the (10·2) peak of about 4×10^3 counts/8 min above background. In fact, as shown in Fig. 1, the observed (10·2) ice Ih line ($2\theta = 24.72°$) has only about one-tenth the calculated intensity, all of which can be attributed to the amount of ice Ih known to be present prior to the transformation. It appears that preferential growth of the crystals, possibly coupled with over-all small particle size and crystal strain, has occurred to limit the intensity of this reflection, and that a greatly broadened line resulted. The calculated position of the centroid of the (111) cubic ice peak coincides (within 0.03° in 2θ) with that of the (00·2) hexagonal peak. It appears that line broadening is responsible for the fact that the lines in the ice Ic–ice Ih mixture are unresolved while the triplet of ice Ih prepared from ice II (which covers the same range of 2θ) is well resolved.

It is well known that crystals smaller than approximately 1000 Å give rise to broadened peaks in the diffraction spectrum.[17] A particle size of about 400 Å was found for ice Ic transformed from vitreous ice.[6] In Table II, application of the Scherrer formula, $t = C\lambda/B \cos\theta$, has been made in a particle-size analysis of ice Ic prepared from ice II. In this expression, t is the crystal thickness in angstroms, C is a constant, ~ 0.9, λ is the wavelength in angstroms of the radiation, B^2 is the difference between the square of the observed linewidth (full width at half-height) and the square of the linewidth expected for large particles from the known diffractometer resolution, and θ is the Bragg angle. Although great accuracy is not to be expected in the application of this expression in the present case, because of the possibility of the presence of a range of crystal sizes and the lack of sphericity of the crystals, it nevertheless serves to provide an estimate of the mean crystal size. As shown in Table II, an analysis of the lines in the ice Ic spectrum indicates that

TABLE II. Evaluation of ice Ic particle size from line broadening.[a]

(hkl)	2θ	B (deg)	t (Å)
(111)	17.9	0.45	130
(220)	29.5	0.36	170
(222)	36.3	0.49	130
(331)	46.1	0.71	90
(422)	52.3	0.65	100
(333) (511)	55.7	0.67	100
(440)	61.1	0.46	150
(531)	64.3	0.47	150

[a] Ice Ic prepared by transformation of ice II, 15 min at −65°C.

[17] C. W. Bunn, *Chemical Crystallography* (Clarendon Press, Oxford, England, 1961), Chap. 11.

in this sample prepared by the transformation of ice II, the mean particle size is about 130 Å. It appears that the crystals are of varying thickness depending upon the crystallographic direction examined, as would be expected. However, because of the uncertainties associated with the application of the Scherrer formula, only qualitative differences in thickness are assumed to be indicated.

The ice Ic prepared from ice II was transformed to ice Ih in several stages. The sample was heated from liquid-nitrogen temperature in the n-pentane bath (a) for 15 min at $-65°C$, (b) for 15 min at $-55°C$, and (c) for 30 min at $-52°C$. The neutron-diffraction pattern was recorded at 80°K after each heating period. As indicated by the $(10 \cdot 0)$ linewidth results, the crystal size of ice Ih increased from 310 Å in (a) to 350 Å in (b) and finally to 610 Å in (c). Approximately corresponding increases were also noted from the $(00 \cdot 2)$, $(10 \cdot 1)$, and $(10 \cdot 2)$ reflections. If any particle-size growth occurred at the temperature of liquid nitrogen, it was exceedingly small since linewidths in both the ice Ic and Ih patterns were reproducible even after the lapse of many days at this temperature.

The fact that cubic ice was not produced in significant amounts by the quenching of aqueous (D_2O) solutions of $FeCl_2$ or KCl is of interest. It is possible that the ^{57}Fe nuclei in the Mössbauer experiments[10] were influenced by strains in the crystal lattice induced by quenching the solution in liquid nitrogen. The neutron-diffraction spectrum clearly indicates the lattice is principally hexagonal in character. Although traces of ice Ic conceivably could be formed, if the Mössbauer spectrum is influenced more than a trace of ice Ic would appear to be required. Changes in the field gradient around the ^{57}Fe caused by crystal strains seems more probable in view of this neutron-diffraction analysis.

Weltman[11] has based his conclusion of the induced formation of ice Ic in rapidly cooled aqueous KCl solutions on resistivity changes and on the appearance of lines in the x-ray spectrum which are not found in the ice Ih. It appears that this is in error. A computer analysis of the two ices shows intensity differences for various reflections but no *new* lines in the ice Ic spectrum.

Note added in proof: The possibility of demonstrating the existence of a proton-disordered structure in ice Ic from neutron-diffraction results was suggested by the referee. We have shown that the proton-disordered model (O–H distance=1.01 Å, and H–O–H angle= 104.5°) reproduces the observed spectrum with an $R=9.5\%$. A reasonable proton-ordered arrangement, space group $I_4\text{-}md$, with the same angle and distance as the disordered structure is in poor agreement ($R=71\%$) with the experimental pattern. In response to a suggestion that the behavior of the H_2O and D_2O ices may not be the same in the vicinity of the iron nucleus, we have made diffraction measurements on a sample of quenched $0.47M$ $FeCl_2$ in H_2O and find no ice Ic phase present within a detection limit of about 5%.

LCAO–MO–SCF Calculations Using Gaussian Basis Functions. II. BeH₂

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Results of extensive LCAO–MO–SCF calculations on BeH₂ utilizing Gaussian basis functions are presented. It is established that BeH₂ is linear in its ground state, and the equilibrium bond distance has been determined. Force constants and normal frequencies were obtained. Utilizing an accurate estimate of the correlation energy, the dissociation energy of BeH₂ was determined to within the experimental error of the National Bureau of Standards measurement.

I. INTRODUCTION

In this paper we present the results of an intensive LCAO–MO–SCF study of beryllium hydride, BeH₂, which is of great practical interest because of its potential utility as one of the most energetic of high-energy rocket fuels. This molecule has also posed a difficult enigma to experimentalists because of the immense difficulty of obtaining a sample pure enough to allow measurement of an accurate heat of formation. It was in the framework of this question of obtaining the BeH₂ bond dissociation energy (which has beset thermochemists for the past five years) that we undertook to perform accurate LCAO–MO–SCF